

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-159309

(43)Date of publication of application : 12.06.2001

(51)Int.Cl.

F01N 3/08

B01D 53/94

F01N 3/20

(21)Application number : 11-343654

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(22)Date of filing : 02.12.1999

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## (54) EXHAUST EMISSION CONTROL DEVICE

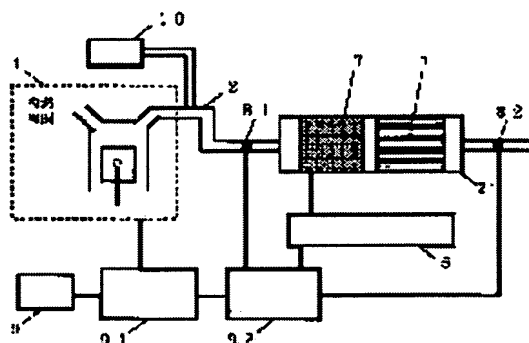
### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide an exhaust emission control device for effectively removing NOX in exhaust gas discharged from an internal combustion engine.

**SOLUTION:** This exhaust emission control device comprises a discharge 7; a catalyst 3; a pulse high voltage generating device 5 to feed a pulse-form high voltage between the electrodes of the discharge device 7, exhaust gas thermometers 81 and 82 situated in a spot situated downstream and a spot situated upper stream from an exhaust pipe case 2';

an internal combustion engine control device 91 to control the operation state of an internal combustion engine 1, a sensor 9 to measure information

necessary for control to the internal combustion engine control device 91, a second internal combustion engine control device 92 to determine whether discharge of the discharge device 7 is started and control the pulse high voltage generating device 5, and a reduction agent adding device 10 to add a reduction agent, necessary to purification of exhaust gas, to a spot situated upper stream from the discharge generating region of an exhaust pipe 2, which are situated, in the order, from a spot situated upper stream of exhaust gas in the exhaust pipe case 2' situated in the exhaust pipe 2 of the internal combustion engine 1, such as a diesel engine.



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LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

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CLAIMS

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[Claim(s)]

[Claim 1] The catalyst which is equipment which purifies the exhaust gas from an internal combustion engine, and was prepared in an internal combustion engine's exhaust pipe, The discharge device made to generate discharge at least in one side of the exhaust gas upstream to this catalyst or this catalyst, The exhaust gas purge which has the improvement function in activity of the catalyst characterized by having the high-voltage power source which applies an electrical potential difference to this discharge device, and reducing-agent addition equipment which adds a reducing agent at least by one side in the exhaust pipe of the exhaust gas upstream rather than the inside of an internal combustion engine's cylinder, or said discharge generating field.

[Claim 2] The exhaust gas purge according to claim 1 which has the gas thermometer which measures exhaust gas temperature, and the control unit which controls discharge voltage and the amount of reducing agents based on the measurement temperature from this thermometer.

[Claim 3] The exhaust gas purge according to claim 1 which has the sensor which detects the information concerning operational status, such as an internal combustion engine's rotational frequency, a load, an inhalation air content, and main-injection fuel quantity, the control unit which controls an internal combustion engine based on the signal from this sensor, and the control unit which controls discharge voltage and the amount of reducing agents based on an internal combustion engine's operation situation.

[Claim 4] The exhaust gas purge according to claim 1 to 3 which has the sensor which detects the amount of hydrocarbons in the exhaust gas from an internal combustion engine in the exhaust gas upstream rather than a discharge field.

[Claim 5] The catalyst which is equipment which purifies the exhaust gas from an internal combustion engine, and was prepared in an internal combustion engine's exhaust pipe, The effectiveness of raising the temperature of exhaust gas by generating discharge at least in one side of the exhaust gas upstream to this catalyst or this catalyst, The discharge device which makes poisoning degradation of a catalyst control according to one or more effectiveness in the effectiveness of activating exhaust gas, the effectiveness of raising the temperature of a catalyst, and the effectiveness of raising the activity of a catalyst, The exhaust gas purge which has the catalyst poisoning degradation control function characterized by having the high-voltage power source which applies an electrical potential difference to this discharge device, and the \*\*\*\*\* degradation condition judging and control means which judge whether it is the condition in which a catalyst tends to carry out poisoning degradation, and control a high-voltage power source.

[Claim 6] The catalyst which is equipment which purifies the exhaust gas from an internal combustion engine, and was prepared in an internal combustion engine's exhaust pipe, The effectiveness of raising the temperature of exhaust gas by generating discharge at least in one side of the exhaust gas upstream to this catalyst or this catalyst, The discharge device which makes poisoning degradation of a sulfur poisoning catalyst recover according to one or more effectiveness in the effectiveness of activating exhaust gas, the effectiveness of raising the temperature of a catalyst, and the effectiveness of raising the activity of a catalyst, The exhaust gas purge which has the catalyst poisoning degradation recovery function characterized by having the high-voltage power source which applies an electrical potential difference to this discharge device, and the poisoning degradation condition judging and control means by which a catalyst judges the condition that

poisoning degradation was carried out, and controls a high-voltage power source.

[Claim 7] The catalyst which is equipment which purifies the exhaust gas from an internal combustion engine, and was prepared in an internal combustion engine's exhaust pipe, The effectiveness of raising the temperature of exhaust gas by generating discharge at least in one side of the exhaust gas upstream to this catalyst or this catalyst, The discharge device which makes poisoning degradation of a catalyst control and recover according to one or more effectiveness in the effectiveness of activating exhaust gas, the effectiveness of raising the temperature of a catalyst, and the effectiveness of raising the activity of a catalyst, The exhaust gas purge which has the catalyst poisoning degradation control and the recovery function characterized by having the high-voltage power source which applies an electrical potential difference to this discharge device, and the poisoning degradation condition judging and control means which judge whether it is in the condition to which the catalyst carried out poisoning degradation of whether it is the condition in which a catalyst tends to carry out poisoning degradation, and control a high-voltage power source.

[Claim 8] The exhaust gas purge according to claim 5 to 7 which has reducing-agent addition equipment which adds a reducing agent at least by one side in the exhaust pipe of the exhaust gas upstream rather than the inside of an internal combustion engine's cylinder, or a discharge generating field.

[Claim 9] Said discharge device is an exhaust gas purge according to claim 1 to 8 characterized by inserting a dielectric into inter-electrode [ which was prepared in the exhaust gas upstream of a catalyst ].

[Claim 10] said discharge device with the tubed insulating material which resembled the exhaust pipe case which consisted of conductive metals at this exhaust pipe case inside, and was prepared by being close The exhaust gas purge according to claim 1 to 8 with which it consists of two or more tabular electrodes prepared by being close to this insulating material, and the ratio of the die length (m) of the circumferencial direction of this electrode and the die length (n) of this inter-electrode circumferencial direction is characterized by being  $m/n=1 / 1 - 1/10$ .

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the equipment which purifies the exhaust gas from an internal combustion engine, and the exhaust gas purge characterized by having a discharge means for recovery of the improvement in activity of a catalyst, control of degradation of a catalyst, and degradation of a catalyst, and a control means especially.

[0002]

[Description of the Prior Art] Electrodischarge treatment is performed to the thing and exhaust gas which are going to carry out reduction removal under existence of HC, using the reduction catalyst of an alumina and a zeolite system as a technique which purifies NOX in the exhaust gas discharged by the internal combustion engine (NO and NO<sub>2</sub>), the gas molecule in exhaust gas is activated, and it is NOX. The technique which is going to improve removal has been proposed. NOX in the exhaust gas discharged by those internal combustion engines In the technique to purify, corona discharge is performed into an internal combustion engine's exhaust pipe, and it is NO by corona discharge NO<sub>2</sub> Raising low-temperature-izing purification activity temperature of a catalyst and purification effectiveness because gas temperature rises by discharge at the same time it oxidizes is known (JP,7-247827,A).

[0003] moreover, as a technique which is going to solve the problem of degradation with the sulfur of a reduction catalyst When an air-fuel ratio is Lean, it is NOX in exhaust gas. NOX which was absorbed, and was absorbed when an air-fuel ratio was rich NOX to emit It is the exhaust gas purge of the internal combustion engine which used the occlusion agent. NOX A sulfur absorbed amount decision means to judge having become more than the specified quantity as which the sulfur absorbed amount absorbed by the occlusion agent was determined beforehand, when it is judged that the sulfur more than the specified quantity was absorbed by it, while setting up an air-fuel ratio richly Invention of the exhaust gas purge of the internal combustion engine having a calorific value increase means to increase the calorific value of the exhaust gas which flows into an exhaust gas purge is indicated. Namely, NOX which carried out sulfur poisoning In order to make sulfur emit and to increase the calorific value of an exhaust gas to an occlusion agent, without heating by an electric heater etc. from the exterior, a flame failure is compulsorily carried out with the Lean flame-failure means, the hydrocarbon (HC) which came out is burned with a catalyst, and exhaust gas temperature is raised, and lag control of the ignition timing is carried out, and it is indicated that it is what raises exhaust gas temperature (JP,10-54274,A).

[0004]

[Problem(s) to be Solved by the Invention] Corona discharge is generated in the above-mentioned internal combustion engine's exhaust pipe, and, thereby, it is NOX in exhaust gas. In invention to purify, the hydrocarbon feeder which adds HC as a reducing agent is installed in the inlet port of a reduction catalyst, and there is especially no equipment that supplies a hydrocarbon to the upstream of corona discharge equipment. It sets, when it does not exist with the case where HC exists, and drawing 20 is NO to NO<sub>2</sub> by exhaust gas temperature and discharge. It is a graph showing relation with the amount which oxidizes. By the way, it is NO by corona discharge NO<sub>2</sub> HC is needed in oxidizing. For this, in the gas by which it is for oxidation reaction of NO to carry out the exactly same reaction as photochemical reaction, and HC does not exist, NO is NO<sub>2</sub>. It is because the

reaction which oxidizes hardly progresses. NO<sub>2</sub> of NO [ from ] when exhaust gas is low temperature under corona discharge at the time of HC existence so that clearly from drawing 20 Although oxidation is accepted, most oxidation is not accepted when HC does not exist. In the above-mentioned invention, since the hydrocarbon feeder which adds HC is installed between corona discharge equipment and a reduction catalyst, HC is not supplied to corona discharge equipment. Therefore, when a fuel burns completely in internal combustion engines, such as a diesel power plant, HC does not exist in exhaust gas, consequently it is NO NO<sub>2</sub> It cannot be made to oxidize. Moreover, NO<sub>2</sub> Although activity temperature can be lowered more while the direction of the rate of purification which also set at the time of reduction, and also decomposed and ionized HC by corona discharge improves, in the above-mentioned invention, since HC does not pass along corona discharge equipment, it cannot carry out decomposition of HC, and ionization, but has the problem that the effectiveness by discharge is not acquired. Furthermore, by adding within an internal combustion engine's cylinder, partial oxidation is carried out and HC as a reducing agent is NOX. Although it is also known that purification effectiveness will increase, there is a problem that this effectiveness cannot be used, either, in the above-mentioned invention.

[0005] Moreover, invention of the above-mentioned internal combustion engine's exhaust emission control device is NOX, although exhaust gas temperature is raised, the temperature of a sulfur poisoning catalyst is raised and sulfur poisoning is recovered. In order to raise the temperature of an occlusion catalyst to the level which can recover sulfur poisoning, a lot of HC is needed, it is required to repeat flame-failure control many times for this reason, and there is a problem to which an internal combustion engine's operational status becomes unstable and to say. Moreover, also when raising exhaust gas temperature by lag control, engine operation balance collapses, engine power changes, and a degree of comfort worsens. Thus, there is a problem that it is difficult to carry out stable transit of the car because operational status changes. Moreover, since it is necessary to also loosen a surrounding exhaust pipe when raising whenever [ catalyst temperature ] by combustion, a temperature rise will take time amount, a fuel useless in the meantime will be consumed, and temperature does not fall conversely shortly after poisoning recovery in the heat capacity which a catalyst has when carrying out anticipated use further, but it is NOX in the meantime. There is also a problem of being in the condition that purification is impossible. It can be told to the approach of raising the temperature of a catalyst by burning HC and recovering sulfur poisoning by it from the above reason that many problems are.

[0006] The place which this invention is made in view of the above-mentioned trouble, and is made into the purpose NOX in the exhaust gas discharged by the internal combustion engine In case it is going to remove good (1) Reducing-agent content exhaust gas and a catalyst are activated, and it is NO<sub>2</sub> of NO. Oxidation, N<sub>2</sub> of NO<sub>2</sub> (2) NOX which returns more effectively Occlusion reduction catalyst, Selection reduction type NOX Control and control that sulfur poisoning arises for catalysts (for example, reduction catalyst of an alumina and a zeolite system), such as a catalyst. (3) It is offering the exhaust gas processor [ like ] which can perform degradation recovery of the sulfur poisoning catalyst which controlled and controlled and sulfur poisoning to (4) catalysts generated which recovers degradation of the generated sulfur poisoning catalyst also in the condition of not losing balance of the above internal combustion engines' operational status.

[0007]

[Means for Solving the Problem] this invention persons are NOX in the exhaust gas discharged by the internal combustion engine. NOX used in case it removes An occlusion reduction catalyst and selection reduction type NOX Catalyst (It may only be hereafter called a "catalyst".) When investigation and research are done about degradation of the catalyst by the relation between the catalysis under reducing-agent existence, and its catalysis and plasma discharge, the phenomenon which sulfur poisoning produces for a catalyst, and its thing, recovery of a sulfur poisoning catalyst, etc., the following is found out and this invention is completed.

[0008] Although the nitrogen oxides (NOX) in the exhaust gas discharged from a [oxidization to NO<sub>2</sub> of NO] diesel power plant etc. have much NO, in the case of a selection reduction catalyst, it is NO<sub>2</sub> from NO. The rate of purification of direction is high (see drawing 9 of above-mentioned JP,7-247827,A, and 10). However, NO<sub>2</sub> of NO Under the environment where HC is required for oxidation since it is the same as that of photochemical reaction, and HC does not exist NO<sub>2</sub>

Oxidation is [ hardly progressing also in a plasma discharge field, i.e., plasma discharge, and ] NO<sub>2</sub> of NO under existence of HC. Oxidation reaction For example, when C<sub>3</sub>H<sub>6</sub> are used as HC, A reaction like  $O + C_3H_6 \rightarrow C_2H_5 + HCOC_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + MHCO + O_2 -$

$\rightarrow CO + HO_2C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2H_2O + NO \rightarrow OH + NO_2$  arises. NO is NO<sub>2</sub>. Oxidize. Therefore, NO is NO<sub>2</sub>. HC is required in order to become (the Suzuki \*\*\*\*, "atmospheric science", the University of Tokyo publication 1979, p.37 - 40 reference).

[Catalytic activity] It is ionized or decomposed when HC passes along a plasma discharge field. Since the temperature of the exhaust gas which the activity of the catalyst in contact with the plasma improves, and catalytic reaction becomes easy to progress, and contacts a catalyst by plasma discharge also rises, NO<sub>x</sub> high from from when the temperature of the exhaust gas discharged from an engine is in a low-temperature region Purification can be obtained, NO<sub>x</sub> In the case of an occlusion reduction catalyst, it is NO<sub>2</sub> from NO. Even if it does not generate plasma discharge at that occlusion of the direction is carried out more to a catalyst at low temperature, and the temperature which the temperature of exhaust gas can purify enough with a catalyst, the rate of purification of exhaust gas is maintainable in the high condition.

[0009] [Sulfur poisoning to catalyst] NO<sub>x</sub> With an occlusion reduction type catalyst NO<sub>x</sub> discharged by the internal combustion engine When carrying out occlusion, NO oxidizes on a catalyst front face, and they are NO<sub>2</sub> and NO<sub>3</sub>. That occlusion is become and carried out, another side, and SO<sub>2</sub> It is SO<sub>2</sub> when it reaches on a catalyst front face. SO<sub>3</sub> It becomes and is NO<sub>3</sub>. Although occlusion is carried out instead The exhaust gas which is a usual internal combustion engine operating range in the state of low temperature (600 degrees C or less) SO<sub>3</sub> by which occlusion was carried out Becoming the cause of it not being returned easily but worsening the occlusion capacity of a catalyst as sulfur poisoning, and NO<sub>2</sub> SO<sub>2</sub> When both sides arrive at a catalyst front face SO<sub>2</sub> It compares and is NO<sub>2</sub>. As opposed to that the occlusion of the direction is easier to be carried out to a catalyst, a catalyst, or a catalyst by the exhaust gas upstream By generating discharge on a suitable electrical potential difference, it is NO<sub>2</sub> alternatively about NO in exhaust gas. It can be made to oxidize, CO generated by plasma discharge by partial oxidation and decomposing in HC component of a reducing agent, or H<sub>2</sub> SO<sub>3</sub> SO<sub>2</sub> Also in that it can emit by carrying out, and the ambient atmosphere place where O<sub>2</sub> does not exist It radical-izes and HC is SO<sub>3</sub>. That a reduction reaction can be promoted and NO<sub>2</sub> SO<sub>2</sub> Since there is a property by which compares and occlusion is quickly carried out to a catalyst, Even if it uses the fuel with which sulfur was contained as that sulfur poisoning becomes occlusion is carried out and is hard to be carried out and a result before sulfur poisoning arises, it can consider as the condition of being hard to carry out sulfur poisoning.

[0010] [About a cure means]

- NO<sub>2</sub> of NO In the condition that HC is not added to the inside of an internal combustion engine's cylinder, or an exhaust pipe, but there is no HC to oxidation, NO is NO<sub>2</sub> also by plasma discharge. Since it is hard to oxidize, it be more nearly required than the plasma discharge field in a cylinder or an exhaust pipe to form the reducing-agent addition equipment which adds a reducing agent (HC) in the exhaust gas upstream, and to add HC.

- It be required to control the generating condition of plasma (responding to height of exhaust gas temperature etc.) discharge about catalytic activity according to an internal combustion engine's condition.

- It be required to establish the \*\*\*\*\* degradation condition judging and control means which controls whether it should judge whether it is in the exhaust gas ambient atmosphere in which a catalyst tends to carry out poisoning to control and control of sulfur poisoning to a catalyst (detection or presumption), and the discharge for poisoning evasion should be generated.

- It be required to establish the poisoning degradation condition judging and control means which controls whether the poisoning degradation condition of a catalyst should be judged (detection or presumption), and the discharge for poisoning recovery should be generated to degradation recovery of a sulfur poisoning catalyst. This invention is completed by finding out the above phenomena and a cure means.

[0011] "Namely, the exhaust gas purge concerning this invention, the catalyst which is equipment which purifies the exhaust gas from an internal combustion engine, and was prepared in an internal

combustion engine's exhaust pipe, The discharge device made to generate discharge at least in one side of the exhaust gas upstream to this catalyst or this catalyst, exhaust gas purge which has the improvement function in activity of the catalyst characterized by having the high-voltage power source which applies an electrical potential difference to this discharge device, and reducing-agent addition equipment which adds a reducing agent at least by one side in the exhaust pipe of the exhaust gas upstream rather than the inside of an internal combustion engine's cylinder, or a discharge generating field. " (claim 1) -- it considers as a summary (matter which specifies invention). Moreover, the gas thermometer with which the exhaust gas purge concerning this invention measures - exhaust gas temperature, The sensor which detects the information concerning operational status, such as a rotational frequency of having the control unit which controls discharge voltage and the amount of reducing agents based on the measurement temperature from this thermometer (claim 2), and - internal combustion engine, a load, an inhalation air content, and main-injection fuel quantity, It is based on the control unit which controls an internal combustion engine based on the signal from this sensor, and an internal combustion engine's operation situation. Discharge voltage, It has [ having the control unit which controls the amount of reducing agents (claim 3), ] the sensor which detects the amount of hydrocarbons in the exhaust gas discharged by - internal combustion engine in the exhaust gas upstream rather than a discharge field (claim 4), - The above-mentioned discharge device inserts a dielectric into inter-electrode [ which was prepared in the exhaust gas upstream of a catalyst ] (claim 9), - the above-mentioned discharge device with the tubed insulating material which resembled the exhaust pipe case which consisted of conductive metals at this exhaust pipe case inside, and was prepared by being close It consists of two or more tabular electrodes prepared by being close to this insulating material, and the ratio of the die length (m) of the circumferencial direction of this electrode and the die length (n) of this inter-electrode circumferencial direction can make at least one of the being [ it /  $m/n=1 / 1 - 1/10$  ] (claim 10) \*\*s the matter which specifies invention.

[0012] "Moreover, the exhaust gas purge concerning this invention, the catalyst which is equipment which purifies the exhaust gas from an internal combustion engine, and was prepared in an internal combustion engine's exhaust pipe, The effectiveness of raising the temperature of exhaust gas by generating discharge at least in one side of the exhaust gas upstream to this catalyst or this catalyst, The discharge device which makes poisoning degradation of a catalyst control according to one or more effectiveness in the effectiveness of activating exhaust gas, the effectiveness of raising the temperature of a catalyst, and the effectiveness of raising the activity of a catalyst, exhaust gas purge which has the catalyst poisoning degradation control function characterized by having the high-voltage power source which applies an electrical potential difference to this discharge device, and the \*\*\*\*\* degradation condition judging and control means which judge whether it is the condition in which a catalyst tends to carry out poisoning degradation, and control a high-voltage power source. " (claim 5) -- it considers as a summary (matter which specifies invention). Moreover, the thing for which the exhaust gas purge concerning this invention has the internal combustion engine control unit which controls - internal combustion engine's operational status, - It has reducing-agent addition equipment which adds a reducing agent at least by one side in the exhaust pipe of the exhaust gas upstream rather than the inside of an internal combustion engine's cylinder, or a discharge generating field (claim 8), - The above-mentioned discharge device inserts a dielectric into inter-electrode [ which was prepared in the exhaust gas upstream of a catalyst ] (claim 9), - the above-mentioned discharge device with the tubed insulating material which resembled the exhaust pipe case which consisted of conductive metals at this exhaust pipe case inside, and was prepared by being close It consists of two or more tabular electrodes prepared by being close to this insulating material, and the ratio of the die length (m) of the circumferencial direction of this electrode and the die length (n) of this inter-electrode circumferencial direction can make at least one of the being [ it /  $m/n=1 / 1 - 1/10$  ] (claim 10) \*\*s the matter which specifies invention.

[0013] "Moreover, the exhaust gas purge concerning this invention, the catalyst which is equipment which purifies the exhaust gas from an internal combustion engine, and was prepared in an internal combustion engine's exhaust pipe, The effectiveness of raising the temperature of exhaust gas by generating discharge at least in one side of the exhaust gas upstream to this catalyst or this catalyst, The discharge device which makes poisoning degradation of a sulfur poisoning catalyst recover



according to one or more effectiveness in the effectiveness of activating exhaust gas, the effectiveness of raising the temperature of a catalyst, and the effectiveness of raising the activity of a catalyst, exhaust gas purge which has the catalyst poisoning degradation recovery function characterized by having the high-voltage power source which applies an electrical potential difference to this discharge device, and the poisoning degradation condition judging and control means by which a catalyst judges the condition that poisoning degradation was carried out, and controls a high-voltage power source. " (claim 6) -- it considers as a summary (matter which specifies invention). Moreover, the thing for which the exhaust gas purge concerning this invention has the internal combustion engine control unit which controls - internal combustion engine's operational status, - It has reducing-agent addition equipment which adds a reducing agent at least by one side in the exhaust pipe of the exhaust gas upstream rather than the inside of an internal combustion engine's cylinder, or a discharge generating field (claim 8), - The above-mentioned discharge device inserts a dielectric into inter-electrode [ which was prepared in the exhaust gas upstream of a catalyst ] (claim 9), - the above-mentioned discharge device with the tubed insulating material which resembled the exhaust pipe case which consisted of conductive metals at this exhaust pipe case inside, and was prepared by being close It consists of two or more tabular electrodes prepared by being close to this insulating material, and the ratio of the die length (m) of the circumferencial direction of this electrode and the die length (n) of this inter-electrode circumferencial direction can make at least one of the being [  $it / m/n = 1 / 1 - 1/10$  ] (claim 10) \*\*s the matter which specifies invention.

[0014] "Moreover, the exhaust gas purge concerning this invention, the catalyst which is equipment which purifies the exhaust gas from an internal combustion engine, and was prepared in an internal combustion engine's exhaust pipe, The effectiveness of raising the temperature of exhaust gas by generating discharge at least in one side of the exhaust gas upstream to this catalyst or this catalyst, The discharge device which makes poisoning degradation of a catalyst control and recover according to one or more effectiveness in the effectiveness of activating exhaust gas, the effectiveness of raising the temperature of a catalyst, and the effectiveness of raising the activity of a catalyst, The exhaust gas purge which has the catalyst poisoning degradation control and the recovery function characterized by having the high-voltage power source which applies an electrical potential difference to this discharge device, and the poisoning degradation condition judging and control means which judge whether it is in the condition to which the catalyst carried out poisoning degradation of whether it is the condition in which a catalyst tends to carry out poisoning degradation, and control a high-voltage power source. " (claim 7) -- it considers as a summary (matter which specifies invention). Moreover, the thing for which the exhaust gas purge concerning this invention has the internal combustion engine control unit which controls - internal combustion engine's operational status, - It has reducing-agent addition equipment which adds a reducing agent at least by one side in the exhaust pipe of the exhaust gas upstream rather than the inside of an internal combustion engine's cylinder, or a discharge generating field (claim 8), - The above-mentioned discharge device inserts a dielectric into inter-electrode [ which was prepared in the exhaust gas upstream of a catalyst ] (claim 9), - The tubed insulating material prepared by the above-mentioned discharge device being close to the exhaust pipe case and this exhaust pipe case inside which consisted of conductive metals, It consists of two or more tabular electrodes prepared by being close to this insulating material, and the ratio of the die length (m) of the circumferencial direction of this electrode and the die length (n) of this inter-electrode circumferencial direction can make at least one of the being [  $it / m/n = 1 / 1 - 1/10$  ] (claim 10) \*\*s the matter which specifies invention.

[0015]

[Embodiment of the Invention] In the equipment with which this invention purifies the exhaust gas from an internal combustion engine rather than the plasma discharge field in (1) cylinder or an exhaust pipe The exhaust gas upstream The reducing-agent addition equipment which adds a reducing agent (HC) (for it to only be hereafter called the "upstream") is formed, (2) The generating condition of plasma discharge is controlled according to an internal combustion engine's condition, (3) The \*\*\*\*\* degradation condition judging and control means which judges and controls whether it should judge whether it is in the exhaust gas ambient atmosphere in which a catalyst tends to carry out poisoning (detection or presumption), and the discharge for poisoning evasion should be

generated are established, (4) The poisoning degradation condition of a catalyst is judged (detection or presumption), and it is characterized by establishing the poisoning degradation condition judging, control means, etc. which judges and controls whether the discharge for poisoning recovery should be generated and to carry out.

[0016] This invention is not limited by the gestalt of the following operations although the gestalt of operation of this invention is explained with reference to a drawing below at a detail. Drawing 1 is the schematic diagram of the 1st operation gestalt of the exhaust gas purge of the internal combustion engine concerning this invention. That is, it is the schematic diagram of the exhaust gas purge which has a catalytic activity function. Exhaust pipe case 2' by which this internal combustion engine's exhaust gas purge was prepared in the exhaust pipe 2 of the internal combustion engines 1, such as a diesel power plant, the exhaust pipe case 2 -- the thermometers 81 and 82 for measuring the temperature of exhaust gas prepared in the upstream and the downstream of 'the discharge device 7 by which sequential arrangement was carried out from the upstream inside, a catalyst 3 and the pulse height electrical-potential-difference generator 5 which supplies the pulse-like high voltage to inter-electrode [ of a discharge device 7 ], and the exhaust pipe case 2' -- It decides whether start discharge of the sensor 9 which measures information required for the internal combustion engine control unit 91 and the internal combustion engine control unit 91 which control an internal combustion engine's 1 operational status at control, and a discharge device 7. It consists of reducing-agent addition equipment 10 which adds to the upstream a reducing agent required in order to purify the 2nd internal combustion engine control unit 92 and exhaust gas which control the pulse height electrical-potential-difference generator 5 rather than the discharge generating field of an exhaust pipe 2. The internal combustion engine control device 91 controls an internal combustion engine's 1 operational status based on signals, such as the amount of accelerators measured by the sensor 9, an engine speed, and cooling water temperature. You may presume from an internal combustion engine's operational status instead of measuring exhaust gas temperature directly. In that case, a thermometer 81 is omissible. Moreover, the temperature in a catalyst 3 may be measured instead of measuring the exhaust-gas temperature from catalyst back (catalyst outlet) with a thermometer 82. Moreover, the equipment which adds a reducing agent (HC) in a cylinder may be used instead of the reducing-agent addition equipment 10 which adds a reducing agent to the upstream rather than the discharge generating field of an exhaust pipe 2. In any case, since HC is added by the upstream rather than a discharge generating field, required HC will be supplied in a discharge field, and HC will be added at the place whose exhaust gas temperature is an elevated temperature, and HC is evaporated easily and it comes to be mixed with homogeneity in exhaust gas. Furthermore, it may be made to generate in a catalyst 3 instead of generating discharge in the upstream of a catalyst 3, and the reaction on the front face of a catalyst is promoted in this case, purification activity can be raised more, and it is NO<sub>2</sub> in exhaust gas low temperature. It is high NO<sub>x</sub> by the synergistic effect of the effectiveness by the occlusion to a catalyst, and the activity effectiveness of the reaction on the front face of a catalyst. The rate of purification is obtained.

[0017] Drawing 2 is drawing showing an example of the concrete configuration of a discharge device 7, and drawing 3 is X of drawing 2, and X cutting sectional view. 101 is constituted from the exhaust pipe case by the conductive metal, is grounded and becomes cathode. 102 is the insulating material prepared in the exhaust pipe case 101, is made from the ceramic or the quartz and is close with the metaled exhaust pipe case 101. 103 is a conductive anode plate electrode, and is been [ 103 / it ] close and prepared inside an insulating material 102. The ratio of the die length (m) of the circumferencial direction of an electrode and the die length (n) of an inter-electrode circumferencial direction is set as the suitable value between  $m/n=1/1 - 1/10$ . Lead wire is connected with the electrode 103 from the plug 105, and the high voltage is supplied from the pulse height electrical-potential-difference generator 5. 104 is a spacer, and it is installed in the center section so that exhaust gas may pass near the electrode. It is fixed to the exhaust pipe case 101 by the insulator 106, and a spacer 104 is in an insulating condition in the exhaust pipe case 101 and the anode plate electrode 103.

[0018] Next, purification of the exhaust gas by the above-mentioned internal combustion engine's exhaust gas purge is explained to a detail with reference to a drawing. Drawing 4 is a graph showing the relation between exhaust gas temperature, the yield (TNO<sub>x</sub>) of nitrogen oxides, and equivalent

ratio, drawing 5 is a graph showing the relation between an engine speed and an unburnt [ fuel quantity / injection ] HC concentration line, drawing 6 is a graph showing the relation between exhaust gas temperature and the yield (TNOX) of nitrogen oxides, and drawing 7 is drawing showing the relation between the yield of nitrogen oxides, and the pulse voltage impressed to a discharge device.

[0019] An engine speed, an inhalation air content, and the load and fuel quantity that were measured by [control of reducing-agent addition] sensor 9 are transmitted to the 2nd internal combustion engine control unit 92 as a signal of the 1st internal combustion engine control unit 91. In the 2nd internal combustion engine control unit 92, equivalent ratio is computed from an inhalation air content and fuel quantity, and the yield (TNOX) of nitrogen oxides is calculated on the map shown in drawing 4 from the obtained equivalent ratio and the exhaust gas temperature measured with the thermometer 81. Moreover, in the 2nd internal combustion engine control device 92, the amount (THCmap) of unburnt HC is computed using the map shown in drawing 5 from an engine speed and fuel quantity, and the amount (THC) of unburnt HC which added amendment by cooling water temperature (Tw) by the degree type, and amended it is calculated.

$THC = THC_{map} - aaTw + bb$  (aa and bb are a constant)

Next, with the 2nd internal combustion engine control unit 92, it is TNOX. From THC, the amount (AHC) of HC added from reducing-agent addition equipment is computed, and the amount of HC to add is controlled by the degree type.

$AHC = aTNOX - THC$  (a is a constant)

In addition, the amount of unburnt HC in an exhaust pipe is NOX in the exhaust pipe between a discharge device and an internal combustion engine, although presumed from a rotational frequency, fuel oil consumption, and cooling water temperature. A sensor and HC sensor may be attached and measured directly. Moreover, the amount of HC (THCmap) may form and measure a sensor directly in an exhaust pipe. The amount (AHC) of HC added from reducing-agent addition equipment is also controllable based on the measurement temperature from the gas thermometer which measures exhaust gas temperature. That is, exhaust gas temperature becomes an elevated temperature, discharge is stopped by the temperature region to which exhaust gas purification goes only with a catalyst, and the amount of reducing agents is also restricted only to a complement by the exhaust gas purification by the catalyst in it. When such, it can control only based on the measurement temperature from the gas thermometer which measures exhaust gas temperature.

[0020] The exhaust gas temperature of [control of discharge voltage] catalyst outlet is measured with a thermometer 82, and it judges whether in the 2nd internal combustion engine control unit 92, discharge is generated from the yield (TNOX) of the nitrogen oxides obtained as mentioned above, and the exhaust gas temperature measured with the thermometer 82. Namely, TNOX When the temperature of the exhaust gas which reached and was measured with the thermometer 82 is contained in the field (for this field there is little effectiveness of a catalyst 3 and whenever [ catalyst temperature ] is NOX in exhaust gas at low temperature it is a field with many amounts) of (i) in drawing 6 , it discharges to exhaust gas, and it is NO NO2 A reducing agent is also made to disassemble and ionize while making it oxidize. By this discharge, it is NOX. NO2 NOX which is made to shift reaction temperature to a low temperature side while carrying out and making it stick to a catalyst 3, and is discharged An amount can be reduced. Moreover, TNOX And when the exhaust gas temperature measured with the thermometer 82 is contained in the field (this field is NOX there are few amounts, or it is the field where catalytic activity is acquired since whenever [ catalyst temperature ] is in a high condition) of (ii) in drawing 6 , he stops discharge and leaves purification to the capacity of a catalyst. Thereby, spark discharge energy can be saved. In the 2nd internal combustion engine control unit 92, while judging whether the above-mentioned discharge is generated, the pulse voltage supplied to a discharge device 7 from the pulse height electrical-potential-difference generator 5 according to drawing 7 is determined, and the signal is sent to the pulse height electrical-potential-difference generator 5. In the pulse height electrical-potential-difference generator 5 which received the signal, a pulse voltage is supplied to a discharge device 7 according to the signal. In a discharge device 7, if the high voltage is applied to the electrode shown by drawing 2 , the plasma will occur into the part of n in drawing 3 . In order to generate the plasma efficiently, the relation between the die length (m) of the circumferencial direction of an electrode

and the die length (n) of an inter-electrode circumferencial direction is important, and it is necessary to change this by the system (NOX to which this invention is applied purification system) made into a technical problem. In the example shown in the drawing, the ratio is  $m/n=1/1$ . In addition, the cathode electrode 101 and the anode plate electrode 103 can generate the plasma having stuck to the insulator 102 efficiently [ direction ]. Moreover, instead of carrying out based on the signal of both the information concerning internal combustion engines, such as an engine speed which measured control of the above discharge voltage by the sensor 9, an inhalation air content, a load, and fuel quantity, and the signal from a thermometer 81 and 82 grades which measured exhaust-gas temperature, exhaust gas temperature may become an elevated temperature and you may carry out in the temperature region to which exhaust gas purification goes only with a catalyst only based on the signal from a thermometer 81 and 82 grades which measured exhaust-gas temperature.

[0021] Drawing 8 is NOX in a catalyst outlet [ as opposed to / technique / (exhaust gas purge without a discharge device) / this invention and / conventional / exhaust gas temperature ]. It is the graph which showed the amount. This graph is NOX in a catalyst outlet when an internal combustion engine's load is raised gradually and the exhaust gas temperature from an internal combustion engine rises gradually. An amount is plotted. With the conventional technique only using drawing 8 to a catalyst, exhaust gas is NOX in a low-temperature field (field in [ B ] drawing 8 ). For that sufficient purification will start if the activity of a catalyst comes to appear and it becomes the field of D as hardly progressing and exhaust gas temperature rise, and this reason, most purification is NOX in a low-temperature region. It is clear that purification is not carried out. on the other hand, in this invention, in the field of B of exhaust gas low temperature without catalytic activity NO is NO<sub>2</sub>. Although the activity of a catalyst will begin to work if whenever [ catalyst temperature ] goes up with the rise of that adsorb into a catalyst and piping (this is adsorbed since the moisture of combustion gas is attached to the interior of piping at the time of low temperature), and the discharge from a catalyst outlet is controlled by being carried out, and exhaust gas temperature It is clear that catalytic activity has arisen from from by it being part-decomposed by discharge and HC being ionized when exhaust gas is low temperature as compared with the case where there is no discharge. Moreover, although catalytic activity is not enough acquired in the conventional technique without discharge in the field of B in drawing 8 , since sufficient activity of a catalyst is acquired even if it does not operate a discharge device in hot temperature from that catalytic activity is acquired by the discharge device in this invention, and an A point, it is clear that the same purification property is acquired also in the conventional technique. Thus, according to this invention, it becomes possible to offer the always high rate of purification also to the exhaust gas temperature which always changes. In addition, when discharge purifies exhaust gas, the suitable current corresponding to the temperature of the exhaust gas, a presentation, and a flow rate (residence time under discharge) and an electrical potential difference exist. Therefore, it is also possible by guessing the exhaust gas temperature at that time, a presentation, and a flow rate from the signal of engine operational status, and measuring in a direct exhaust pipe to control to apply the electrical potential difference and current which were most suitable for the exhaust gas condition at that time. By such control, power consumption can be stopped and exhaust gas can be purified efficiently.

[0022] Drawing 9 is the schematic diagram of the 2nd operation gestalt of the exhaust gas purge of the internal combustion engine concerning this invention. That is, the schematic diagram of the exhaust gas purge of the internal combustion engine which has a poisoning control function is shown. Drawing 10 shows other structures of the electrode section of the 2nd operation gestalt of the exhaust gas purge of the internal combustion engine concerning this invention. This internal combustion engine's exhaust gas purge The operational status of the electrodes 42 and 43 of the disc-like pair which has the permeability prepared in the upstream of the catalyst 3 prepared in an internal combustion engine's 1 exhaust pipe 2, and a catalyst 3, the electrode 42 of a pair, the pulse height electrical-potential-difference generator 5 that supplies the pulse-like high voltage among 43, and an internal combustion engine 1 It judges whether it is in the condition that poisoning of the sensor 9 and catalyst 3 which measure information required for the internal combustion engine control unit 91 and the internal combustion engine control unit 91 to control at control is easy to be carried out (detection or presumption). Rather than the electrodes 42 and 43 and catalyst 3 of a pair which are used as an ingredient for the \*\*\*\*\* degradation condition judging and the control means 93, and

the \*\*\*\*\* degradation condition judging and the control means 93 which control the pulse height electrical-potential-difference generator 5 to judge, the gas temperature of the upstream, It consists of thermometers 81 and 82 which measure the exhaust gas temperature after passing a catalyst. In addition, a dielectric 41 (for example, alumina) can also be inserted so that it may be easy to produce discharge (plasma) between the electrode 42 of a pair, and 43. Moreover, with above equipment, instead of the electrodes 42 and 43 of the disc-like pair which has the permeability prepared in the upstream of a catalyst 3, the tubed electrode 45 may be formed in the periphery of an exhaust pipe 2 in the electrode 44 and electrode 44 of the shape of a rod prepared in the upstream of a catalyst 3, and the corresponding location as shown in drawing 10 . Moreover, in the condition that there is no HC although the reducing-agent addition equipment which adds a reducing agent (HC) to the inside of an internal combustion engine's cylinder or an exhaust pipe is not formed with above equipment, NO is NO<sub>2</sub> by discharge. Since it is hard to oxidize, it is also possible to form the reducing-agent addition equipment which performs HC addition into a cylinder or HC addition into an exhaust pipe. [0023] Next, purification of the exhaust gas by the above-mentioned internal combustion engine's exhaust gas purge is explained to a detail with reference to a drawing. Drawing 11 is drawing showing the relation between the mean temperature of the exhaust gas before and behind a catalyst, and the amount of the sulfur in exhaust gas. The internal combustion engine control computer 91 controls an internal combustion engine's 1 operational status based on signals, such as the amount of accelerators measured by the sensor 9, an engine speed, and cooling water temperature. The amount of exhaust gas from injection fuel quantity, an engine speed, and the amount of EGR(s) is transmitted to the \*\*\*\*\* degradation condition judging means 93 at coincidence. Furthermore, the signal from thermometers 81 and 82 established before and after the catalyst is inputted into the \*\*\*\*\* degradation condition judging means 93. With the \*\*\*\*\* degradation condition judging means 93, the sulfur concentration in exhaust gas is presumed from the injected fuel and an inhalation air content. Since the amount of sulfur contained in the fuel is almost fixed, the amount of sulfur (sulfur concentration) can be presumed from fuel quantity. Furthermore, it asks for the mean temperature of thermometers 81 and 82. And when it goes into Field C in the graph shown by drawing 11 , it judges with the \*\*\*\*\* degradation condition judging means 93 being in the condition that poisoning of the catalyst is easy to be carried out, and a discharge generating signal is sent to the pulse height electrical-potential-difference generator 5. The pulse height electrical-potential-difference generator 5 will generate a high-voltage pulse, if a signal is received, applies a high-voltage pulse to exhaust gas through electrodes 42 and 43, and generates discharge. Although the pulse height electrical-potential-difference generator made to generate the high voltage as a high-voltage pulse with more high effectiveness was used here, a constant-pressure high-voltage transformer assembly is sufficient.

[0024] Drawing 12 is NOX [ as opposed to / technique / (how not to use the restraint of sulfur poisoning) / this invention and / conventional / a time ] of a catalyst. It is the graph which showed absorptance (occlusion possible amount). Drawing 12 is NOX within a catalyst. NOX when returning once Change (NOX of the catalyst after regenerating change of the amount of occlusion) of the amount of occlusion is shown to a time. In this invention, it crosses to long duration more, and is NOX. With the conventional technique, it understands to there being absorptance that poisoning is carried out to sulfur and it becomes impossible to absorb immediately. From drawing 12 , it is distinct that the degradation stage as a catalyst is sharply improvable in this invention. this -- NOX in an occlusion reduction catalyst, NO discharged by the internal combustion engine oxidizes on a catalyst front face -- having -- NO<sub>2</sub> and NO<sub>3</sub> although occlusion is become and carried out -- another side -- general -- SO<sub>2</sub> SO<sub>3</sub> becoming -- NO<sub>3</sub> It is thought that occlusion is carried out instead. Moreover, by discharge, it is SO<sub>2</sub>. Oxidation (NO->NO<sub>2</sub>) of NO tends to progress rather than oxidation (SO<sub>2</sub> ->SO<sub>3</sub>). At this time, it is NO<sub>2</sub>. When a catalyst is reached SO<sub>2</sub> Compare, the occlusion of the direction of NO<sub>2</sub> is easier to be carried out to a catalyst, and it sets to this invention there. By discharge, only NO in exhaust gas is NO<sub>2</sub>. It is SO<sub>2</sub>, in order to oxidize and to reach a catalyst. It compares and is NO<sub>2</sub>. It is thought that sulfur poisoning becomes occlusion of the direction is carried out to a catalyst, consequently is hard to be carried out.

[0025] Drawing 13 is drawing showing the schematic diagram of the 3rd operation gestalt of the exhaust gas purge of the internal combustion engine concerning this invention. That is, the schematic

diagram of the exhaust gas purge of the internal combustion engine which has a poisoning recovery function is shown. This internal combustion engine's exhaust gas purge is prepared in the form which sandwiches the catalyst 3 prepared in the internal combustion engine 1 and the exhaust pipe 2, and a catalyst 3. For a catalyst 3, the high voltage The sensor 9 and the poisoning degradation condition of a catalyst 3 which measure information required for the pulse height electrical-potential-difference generator 5 which supplies the pulse-like high voltage to the electrodes 4 and 4 to cover, the internal combustion engine control unit 91 which controls an internal combustion engine's 1 operational status, and the internal combustion engine control unit 91 at control are judged (detection or presumption). As information for the poisoning degradation condition judging and the control means 94, and the poisoning degradation condition judging and the control means 94 which control the pulse height electrical-potential-difference generator 5 to judge a poisoning degradation condition It consists of reducing-agent addition equipment 10 which adds a reducing agent required in order to recover the thermometer 8 and poisoning degradation catalyst which measure the gas temperature of the catalyst entry to be used in an internal combustion engine's 1 cylinder. In addition, it is very good instead of reducing-agent addition equipment 10 in the form which adds an additive in a cylinder by control of an internal combustion engine 1. Moreover, the reducing-agent addition equipment 10 which adds a reducing agent may be formed in the upstream rather than a catalyst not within a cylinder but within the exhaust pipe 2 of an internal combustion engine outlet. [0026] Next, recovery control of sulfur is explained to a detail. Drawing 14 shows the judgment flow chart of sulfur poisoning. It is NOX as an internal combustion engine 1 as a catalyst 3 for removing the injurious ingredient in exhaust gas for a diesel power plant. It is NOX when it is with an occlusion reduction catalyst. With the sulfur with which an occlusion reduction catalyst is included in a fuel, poisoning is carried out and the engine performance may deteriorate. Sulfur degradation of a catalyst is decided from the amount of the sulfur in the exhaust gas which passed the catalyst, the temperature of the exhaust gas at that time, and the equivalent ratio of exhaust gas. A poisoning degradation condition judging and a control means 94 obtain an engine rotational frequency, the amount of EGR(s), and injection fuel quantity from the internal combustion engine control device 91 first. An inhalation air content (GA) is computed from an engine speed (rpm) and the amount (Gegr) of EGR(s), and it judges whether an exhaust gas is in a rich condition from injection fuel quantity (fuel), and whether it is in the Lean condition. This value is set to Lrich.

$$Lrich = f(rpm, Gegr, Fuel) - (1)$$

[0027] Drawing 15 is a graph showing the relation in the condition that the occlusion of the sulfur is easy to be carried out to exhaust gas temperature and a catalyst. The sulfur occlusion of the occlusion reduction catalyst in lean atmosphere prospers in a certain temperature region, and there is at an exhaust gas low temperature side. [ little ] Moreover, in an exhaust gas pyrosphere, when coming out of a catalyst before occlusion of the sulfur which entered in the catalyst is carried out, the sulfur by which occlusion was carried out is also emitted. In a low-temperature region, in order that a sulphuric occlusion reaction may not progress, there are few amounts by which occlusion is carried out. Drawing 15 is obtained by summarizing the above result, and sulfur's expressing with - (minus) the direction which occlusion is not carried out but is emitted by + (plus) in the condition that poisoning occlusion is easy to be carried out, and writing a graph by setting an axis of abscissa as the exhaust gas temperature to a catalyst. Next, it asks for a coefficient C from drawing 15 using the exhaust gas temperature (Tgas) measured with a thermometer 8.

[0028] Drawing 16 is the graph which expressed the coefficient B showing an exhaust gas flow rate, and the occlusion of the sulfur to a catalyst and the relation of balking with relation with an exhaust gas flow rate. Since the magnitude to which occlusion of the sulfur is carried out in a rich ambient atmosphere is small in the case of an occlusion reduction catalyst, the sulphuric amount of occlusion hardly increases. Moreover, the amount of the sulfur in which an occlusion reduction catalyst carries out occlusion is influenced by the exhaust gas flow rate and the concentration of the sulfur in exhaust gas. About an exhaust gas flow rate (GA), it can compute from an engine speed and the amount of EGR(s), and the concentration (S) of the sulfur in exhaust gas can be computed from the injected amount (fuel) of combustion. When these are expressed with a formula, it is  $GA = f(rpm, Gegr)$ . - (2)  
 $S = f(fuel)$  - (3)

It can express. If there are many amounts of sulfur in exhaust gas even if it is the temperature of the

exhaust gas same with a natural thing, and a flow rate, the amount of sulfur of the amount by which occlusion is carried out from which it increases and is desorbed at the time of an elevated temperature will also decrease. Moreover, as shown in drawing 16, the amount of occlusion of the sulfur to an occlusion reduction catalyst increases, and when an exhaust gas flow rate is large, the occlusion of the sulfur to an occlusion reduction catalyst and the amount from which it can be desorbed become less as a time with few exhaust gas flow rates. It asks for the coefficient B which expresses this relation using drawing 16.

[0029] Drawing 17 is a graph showing the relation between an internal combustion engine's operation time and the addition value of the amount of occlusion sulfur to a catalyst. Next, with reference to the flow chart of drawing 14, the judgment loop formation of sulfur poisoning to an occlusion reduction catalyst is explained. The processing at each step (step 1 - step 7) from a start to termination is as follows.

- Step 1 (S1) : calculation of the concentration (S) of the sulfur in measurement of an engine speed (rpm), the amount (Gegr) of EGR(s), injection fuel quantity (fuel), and exhaust gas temperature (Tgas), an exhaust gas flow rate (GA), and exhaust gas.
- Step 2 (S2) : calculate Lrich from (1) type based on the data measured at step 1, and judge whether exhaust gas is rich.
- step 3(S3): -- it judges with Lean at step 2 -- having -- a case -- a thermometer 8 -- having measured -- temperature -- a radical -- drawing 15 to a coefficient C -- asking . When judged with it being rich at step 2, a judgment loop formation is ended.
- Step 4 (S4) : calculate an exhaust gas flow rate (GA) using a formula (2), and ask for a coefficient B from drawing 16.
- Presume the amount of occlusion sulfur by the following presumed type based on B and C which were calculated at the sulfur concentration (S) for which it asked by the step 5(S5):(3) formula, step 3, and step 4.

$$**S=a*B*(C+S) - (4)$$

Here, a is a constant.

- Integrate \*\*S obtained by the step 6(S6):(4) formula.

$$\text{Stot}(t) = \text{Stot}(t-1) + **S - (5)$$

Here, t expresses time amount. The addition value Stot (t) is a value set as 0 at the time of an internal combustion engine un-operating, and the internal combustion engine is subtracted and added by operation \*\*\*\*\* and (5) types.

- Step 7 (S7) : judge whether Stot (t) is over the threshold A (the value when being set to 80 when the condition that sulfur stopped reaching more than this is set to 100 is set to threshold A) defined independently. When Stot (t) is over the threshold A, a catalyst carries out degradation recovery in the condition of having carried out sulfur poisoning. In being smaller than a threshold A, I hear that Stot (t) still is not in a degradation condition, and it ends this judgment loop formation. This judgment loop formation is calculated by computer which internal combustion engines are working and fixed spacing, and carried, and Stot (t) is calculated.

[0030] When judged with it being in a sulfur poisoning degradation condition, the following degradation recoveries are performed. Namely, by being shown in the above-mentioned judgment loop formation, like, if judged with poisoning degradation of the catalyst 3 being carried out by the poisoning degradation condition judging and the control means 94, the signal will be first told to the pulse height electrical-potential-difference generator 5. In the pulse height electrical-potential-difference generator 5, the high voltage required to give discharge to a catalyst 3 occurs. Although a fixed electrical potential difference is sufficient as this electrical potential difference, its pulse-like electrical potential difference is [ a poisoning restorative effect ] larger. The pulse height electrical potential difference generated with the pulse height electrical-potential-difference generator 5 is applied to a catalyst 3 from an electrode 4. On the other hand, the judgment signal of poisoning degradation is transmitted also to the internal combustion engine control unit 91. In the internal combustion engine control unit 91, operational status is changed so that an exhaust gas component may become conditions convenient to poisoning recovery. NOX In the case of sulfur poisoning of the occlusion reduction catalyst 3, as for the reducing atmosphere, poisoning recovery progresses more rather than a hyperoxia ambient atmosphere. For this reason, the internal combustion engine



control unit 91 controls operational status so that exhaust gas becomes reducing atmosphere. Moreover, a reducing agent (here HC) can also be added in an internal combustion engine cylinder from reducing-agent addition equipment 10.

[0031] The period of this degradation processing is  $T=b \cdot \text{Stot}(t)$ .

It comes out and performs only for T hours expressed. Here, b is a constant. T-hour after, degradation recovery is ended and 0 goes into Stot (t). When the time of a catalyst becomes long, it becomes impossible here, to recover enough, even if it carries out degradation recovery. Then, 0 is not put into Stot (t) after degradation recovery, but an internal combustion engine's operation time is measured, and it is  $\text{Stot}(t)=f(t)$ .

It is also possible to put in the value acquired with the function carried out after degradation recovery. Here, t is a catalyst time. By this approach, the capacity after recovery of a catalyst can be treated more correctly.

[0032] Drawing 18 is NOX at the time of recovering sulfur poisoning with the exhaust gas purge of the internal combustion engine concerning this invention. It is a graph showing change of the amount of occlusion. It is NOX in the time of a catalyst so that clearly from drawing 18. The amount which can carry out occlusion becomes less. If it passes over a certain level, the degradation judging of a catalyst will be made and it will go into degradation recovery operation (A in drawing 18, B). Even the condition in front of poisoning can be made to recover very much only the catalyst front face which could raise activity by ionizing a reducing agent, and carried out poisoning in the poisoning degradation recovery operation by discharge by being made to an elevated temperature for a short time. And NOX almost equal to the condition in front of poisoning The engine performance with the amount of occlusion is obtained. On the other hand, when taking time amount by the Prior art which recovers poisoning degradation only by raising the temperature of a catalyst before the whole catalyst reaches recoverable temperature so that clearly from drawing 18, in the usual internal combustion engine's operating range, it is unrecoverable 100%. Therefore, by the poisoning degradation recovery only by only raising the temperature of a catalyst, as shown in drawing 18, it is NOX of a catalyst. It not only decreases gradually, but there is time amount which poisoning degradation recovery takes, and many or the problem of cutting as the amount of occlusion repeats recovery. On the other hand, in the poisoning degradation recovery by the equipment of this invention using discharge, there is such no problem and the outstanding effectiveness of the ability to make it recovering to the original amount of occlusion for a short time is done so.

[0033] Drawing 19 is a graph showing the relation between exhaust gas temperature required for poisoning degradation recovery, and the amount of recovery at that time. In drawing 19, it is shown that poisoning degradation is recovered well, so that the amount of recovery is large. In being able to ionize a reducing agent near the poisoning side of a catalyst by discharge and being able to raise activity capacity with the equipment of this invention using discharge, since it is locally made near the catalyst front face to an elevated temperature, if it sees from the whole gas temperature, the high amount of recovery can be obtained from a low-temperature region. On the other hand, with the sulfur poisoning degradation recovery technique only by only raising the temperature of the conventional catalyst, in order to recover poisoning degradation completely, even if it is necessary to make exhaust gas temperature into an elevated temperature and carries out recovery below with the exhaust gas temperature, it does not return to the original condition completely. Therefore, there is what has difficult obtaining the exhaust gas temperature made sufficient for recovering completely depending on internal combustion engine's class, and, as for a catalyst, in the case of the catalyst prepared for such an internal combustion engine, the adsorption capacity force will be dropped gradually.

[0034]

[Effect of the Invention] This invention can purify efficiently - internal combustion engine and the nitrogen oxides especially contained in the exhaust gas from a diesel power plant as it was described minutely above. - usually -- coming out - to which catalytic activity can carry out purification from the exhaust gas low-temperature region which is not enough -- usually -- also coming out, when catalytic activity stops discharge in the exhaust gas temperature region which can be demonstrated enough and purifies only with a catalyst As opposed to sulfur poisoning of - catalyst which can suppress loss of energy and which can perform offgas treatment as sulfur poisoning of - catalyst



cannot arise, and can improve the degradation stage as a catalyst sharply While being able to make it recover in a low-temperature region rather than the usual heating approach, the effectiveness which was [ attain / recovery in a short time and the recovery to the condition in front of poisoning ] excellent is done so.

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[Translation done.]

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## DESCRIPTION OF DRAWINGS

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### [Brief Description of the Drawings]

[Drawing 1] It is the schematic diagram of the 1st operation gestalt of the exhaust gas purge of the internal combustion engine concerning this invention.

[Drawing 2] It is drawing showing an example of the concrete configuration of a discharge device 7.

[Drawing 3] They are X of drawing 2, and X cutting sectional view.

[Drawing 4] It is a graph showing the relation between exhaust gas temperature, the yield (TNOX) of nitrogen oxides, and equivalent ratio.

[Drawing 5] It is a graph showing the relation between an engine speed and an unburnt [ fuel quantity / injection ] HC concentration line.

[Drawing 6] It is a graph showing the relation between exhaust gas temperature and the yield (TNOX) of nitrogen oxides.

[Drawing 7] It is drawing showing the relation between the yield of nitrogen oxides, and the pulse voltage impressed to a discharge device.

[Drawing 8] NOX in a catalyst outlet [ as opposed to / technique / this invention and / conventional / exhaust gas temperature ] It is the graph which showed the amount.

[Drawing 9] It is the schematic diagram of the 2nd operation gestalt of the exhaust gas purge of the internal combustion engine concerning this invention.

[Drawing 10] Other structures of the electrode section of the 2nd operation gestalt of the exhaust gas purge of the internal combustion engine concerning this invention are shown.

[Drawing 11] It is drawing showing the relation between the mean temperature of the exhaust gas before and behind a catalyst, and the amount of the sulfur in exhaust gas.

[Drawing 12] NOX [ as opposed to / technique / this invention and / conventional / a time ] of a catalyst It is the graph which showed absorptance.

[Drawing 13] It is drawing showing the schematic diagram of the 3rd operation gestalt of the exhaust gas purge of the internal combustion engine concerning this invention.

[Drawing 14] The judgment flow chart of sulfur poisoning is shown.

[Drawing 15] It is a graph showing the relation in the condition that the occlusion of the sulfur is easy to be carried out to exhaust gas temperature and a catalyst.

[Drawing 16] It is the graph which expressed the coefficient B showing an exhaust gas flow rate, and the occlusion of the sulfur to a catalyst and the relation of balking with relation with an exhaust gas flow rate.

[Drawing 17] It is a graph showing the relation between an internal combustion engine's operation time and the addition value of the amount of occlusion sulfur to a catalyst.

[Drawing 18] NOX at the time of recovering sulfur poisoning with the exhaust gas purge of the internal combustion engine concerning this invention It is a graph showing change of the amount of occlusion.

[Drawing 19] It is a graph showing the relation between exhaust gas temperature required for poisoning degradation recovery, and the amount of recovery at that time.

[Drawing 20] It sets, when it does not exist with the case where HC exists, and it is NO to NO<sub>2</sub> by exhaust gas temperature and discharge. It is a graph showing relation with the amount which oxidizes.

[Description of Notations]

1 Internal Combustion Engine  
2 Exhaust Pipe  
2' Exhaust pipe case  
3 Catalyst  
4 Electrode  
5 Pulse Height Electrical-Potential-Difference Generator  
7 Discharge Device  
8, 81, 82 Thermometer  
9 Sensor  
91 Internal Combustion Engine Control Unit  
92 2nd Internal Combustion Engine Control Unit  
93 \*\*\*\*\* Degradation Condition Judging and Control Means  
94 Poisoning Degradation Condition Judging and Control Means  
10 Reducing-Agent Addition Equipment  
101 Exhaust Pipe Case  
102 Insulating Material  
103 Electrode  
104 Spacer  
105 Plug  
106 Insulator

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[Translation done.]

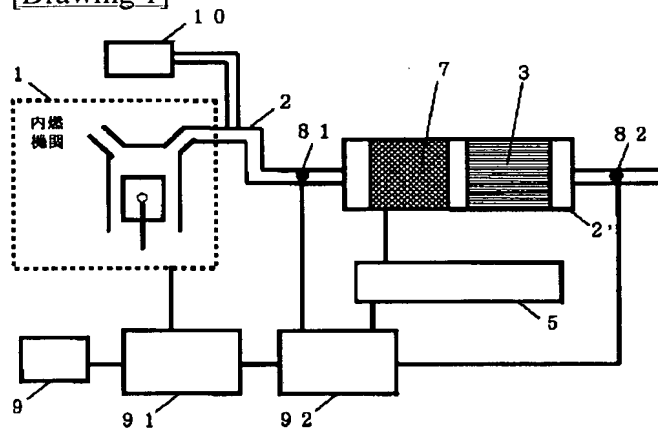
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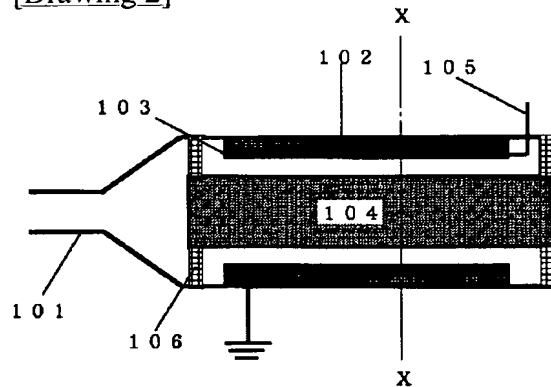
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## DRAWINGS

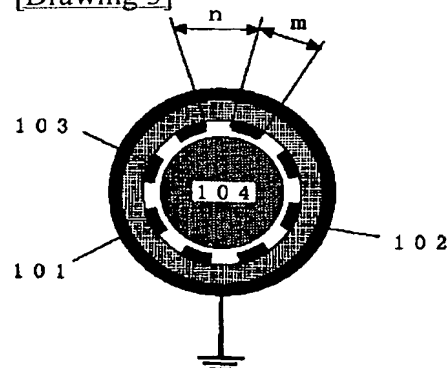
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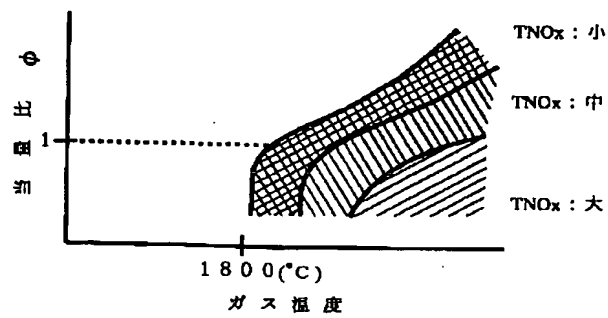
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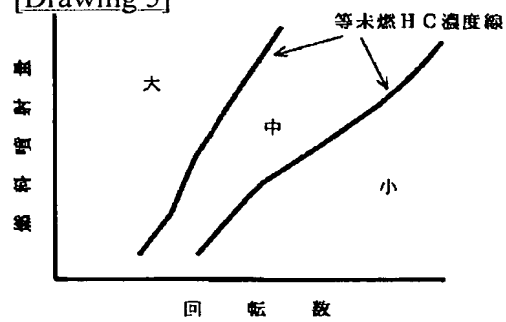
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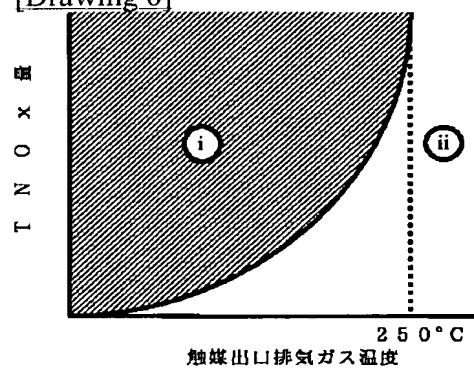
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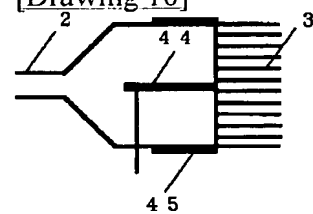
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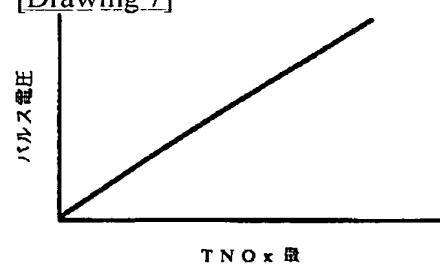
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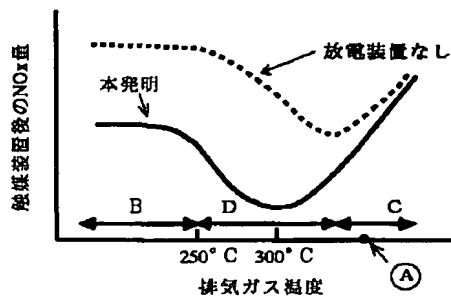
[Drawing 10]



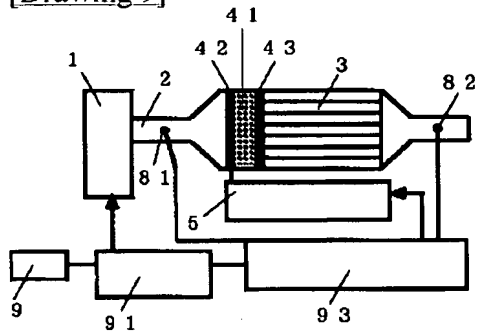
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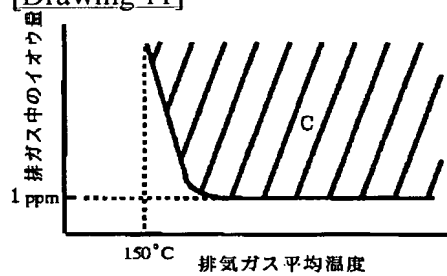
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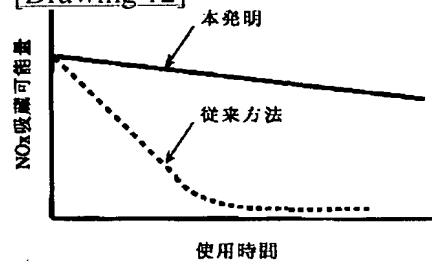
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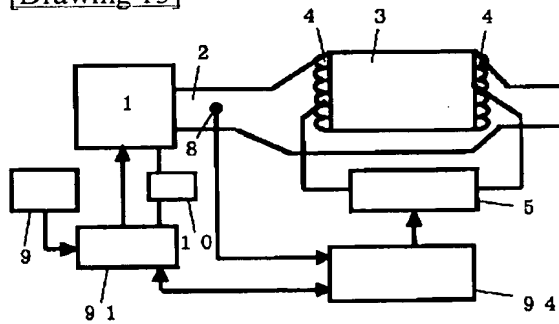
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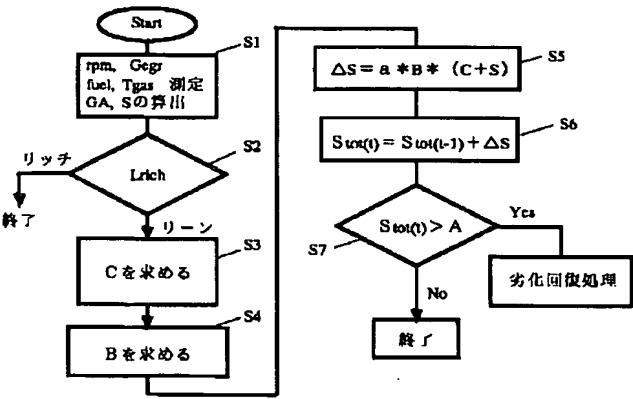
[Drawing 12]



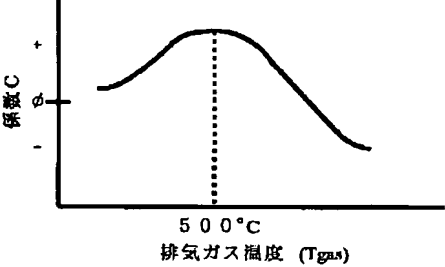
[Drawing 13]



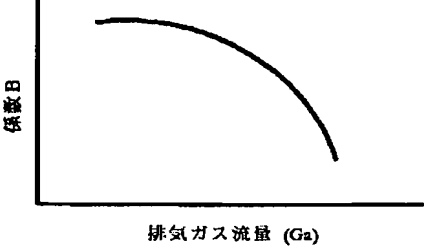
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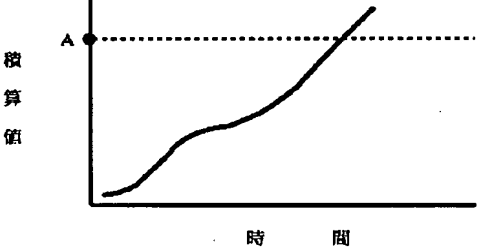
[Drawing 15]



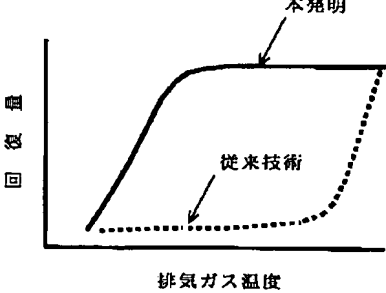
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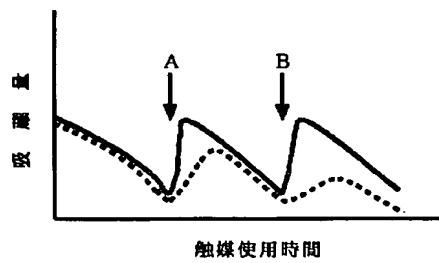
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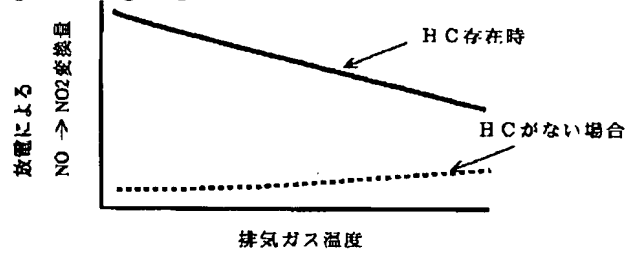
[Drawing 19]



[Drawing 18]



[Drawing 20]



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[Translation done.]



(19) 日本国特許庁 (J P)

## (12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2001-159309

(P2001-159309A)

(43) 公開日 平成13年6月12日 (2001.6.12)

(51) Int.Cl. <sup>7</sup>	識別記号	F I	テームコード* (参考)
F 0 1 N 3/08	Z A B	F 0 1 N 3/08	Z A B B 3 G 0 9 1
			C 4 D 0 4 8
B 0 1 D 53/94		3/20	E
F 0 1 N 3/20		B 0 1 D 53/36	1 0 1 A

審査請求 未請求 請求項の数10 O L (全 13 頁)

(21) 出願番号 特願平11-343654

(22) 出願日 平成11年12月2日 (1999.12.2)

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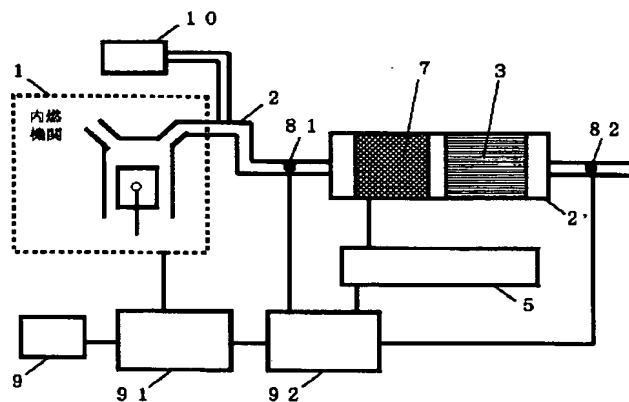
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## (54) 【発明の名称】 排気ガス浄化装置

## (57) 【要約】

【課題】 内燃機関から排出される排気ガス中のNO<sub>x</sub>を効果的に除去することのできる排気ガス浄化装置を提供すること。

【解決手段】 ディーゼルエンジン等の内燃機関1の排気管2に設けられた排気管ケース2'内に、排気ガス上流側から順次配置された放電装置7と触媒3、放電装置7の電極間にパルス状の高電圧を供給するパルス高電圧発生装置5、排気管ケース2'の上流側及び下流側に設けられた排気ガス温度計81、82、内燃機関1の運転状態をコントロールする内燃機関制御装置91、内燃機関制御装置91に制御に必要な情報を計測するセンサー9、放電装置7の放電を開始するかどうかを決め、パルス高電圧発生装置5を制御する第2内燃機関制御装置92、排気ガスを浄化するために必要な還元剤を排気管2の放電発生領域よりも上流側に添加する還元剤添加装置10とから構成されている排気ガス浄化装置。



## 【特許請求の範囲】

【請求項 1】 内燃機関からの排気ガスを浄化する装置であって、内燃機関の排気管に設けた触媒と、該触媒又は該触媒に対して排気ガス上流側の少なくとも一方で放電を発生させる放電装置と、該放電装置に電圧をかける高電圧電源と、内燃機関の筒内又は前記放電発生領域よりも排気ガス上流側の排気管中の少なくとも一方で還元剤を添加する還元剤添加装置とを有することを特徴とする触媒の活性向上機能を有する排気ガス浄化装置。

【請求項 2】 排気ガス温度を計測するガス温度計と、該温度計からの計測温度に基づいて放電電圧、還元剤量を制御する制御装置を有する請求項 1 に記載の排気ガス浄化装置。

【請求項 3】 内燃機関の回転数、負荷、吸入空気量、主噴射燃料量などの運転状態に係る情報を検出するセンサーと、該センサーからの信号を元に内燃機関を制御する制御装置と、内燃機関の運転状況に基づいて放電電圧、還元剤量を制御する制御装置とを有する請求項 1 に記載の排気ガス浄化装置。

【請求項 4】 内燃機関からの排気ガス中の炭化水素量を検出するセンサーを放電領域よりも排気ガス上流側に有する請求項 1～3 のいずれかに記載の排気ガス浄化装置。

【請求項 5】 内燃機関からの排気ガスを浄化する装置であって、内燃機関の排気管に設けた触媒と、該触媒又は該触媒に対して排気ガス上流側の少なくとも一方で放電を発生させることで排気ガスの温度を上昇させる効果、排気ガスを活性化させる効果、触媒の温度を上昇させる効果、触媒の活性を向上させる効果のうちの 1 つ以上の効果により触媒の被毒劣化を抑制せしめる放電装置と、該放電装置に電圧をかける高電圧電源と、触媒が被毒劣化し易い状態か否かを判定し、高電圧電源を制御する易被毒劣化状態判定・制御手段とを有することを特徴とする触媒被毒劣化抑制機能を有する排気ガス浄化装置。

【請求項 6】 内燃機関からの排気ガスを浄化する装置であって、内燃機関の排気管に設けた触媒と、該触媒又は該触媒に対して排気ガス上流側の少なくとも一方で放電を発生させることで排気ガスの温度を上昇させる効果、排気ガスを活性化させる効果、触媒の温度を上昇させる効果、触媒の活性を向上させる効果のうちの 1 つ以上の効果により硫黄被毒触媒の被毒劣化を回復せしめる放電装置と、該放電装置に電圧をかける高電圧電源と、触媒が被毒劣化された状態を判定し、高電圧電源を制御する被毒劣化状態判定・制御手段とを有することを特徴とする触媒被毒劣化回復機能を有する排気ガス浄化装置。

【請求項 7】 内燃機関からの排気ガスを浄化する装置であって、内燃機関の排気管に設けた触媒と、該触媒又は該触媒に対して排気ガス上流側の少なくとも一方で放

電を発生させることで排気ガスの温度を上昇させる効果、排気ガスを活性化させる効果、触媒の温度を上昇させる効果、触媒の活性を向上させる効果のうちの 1 つ以上の効果により触媒の被毒劣化を抑制・回復せしめる放電装置と、該放電装置に電圧をかける高電圧電源と、触媒が被毒劣化し易い状態か否か又は触媒が被毒劣化した状態かを判定し、高電圧電源を制御する被毒劣化状態判定・制御手段とを有することを特徴とする触媒被毒劣化抑制・回復機能を有する排気ガス浄化装置。

10 【請求項 8】 内燃機関の筒内又は放電発生領域よりも排気ガス上流側の排気管中の少なくとも一方で還元剤を添加する還元剤添加装置を有する請求項 5～7 のいずれかに記載の排気ガス浄化装置。

【請求項 9】 前記放電装置は、触媒の排気ガス上流側に設けた電極間に誘電体を挟んだものであることを特徴とする請求項 1～8 のいずれかに記載の排気ガス浄化装置。

20 【請求項 10】 前記放電装置は、導電性金属から構成された排気管ケースと該排気管ケース内面にに密接して設けられた筒状の絶縁物と、該絶縁物に密接して設けられた複数の板状の電極とからなり、該電極の円周方向の長さ (m) と該電極間の円周方向の長さ (n) との比が、 $m/n = 1/1 \sim 1/10$  であることを特徴とする請求項 1～8 のいずれかに記載の排気ガス浄化装置。

## 【発明の詳細な説明】

## 【0001】

30 【発明の属する技術分野】本発明は、内燃機関からの排気ガスを浄化する装置、特に、触媒の活性向上、触媒の劣化の抑制、触媒の劣化の回復のための放電手段、制御手段を有することを特徴とする排気ガス浄化装置に関する。

## 【0002】

40 【従来の技術】内燃機関から排出される排気ガス中の  $\text{NO}_x$  ( $\text{NO}$ ,  $\text{NO}_2$ ) を浄化する技術として、アルミナ、ゼオライト系の還元触媒を用いて  $\text{HC}$  の存在下で還元除去しようとするもの、排気ガスに放電処理を施して排気ガス中の気体分子を活性化し、 $\text{NO}_x$  除去を良くしようとする技術などが提案されてきている。それらの内燃機関から排出される排気ガス中の  $\text{NO}_x$  を浄化する技術の中で、内燃機関の排気管中にコロナ放電を施し、コロナ放電により  $\text{NO}$  を  $\text{NO}_2$  に酸化すると同時に放電によりガス温度が上昇することで、触媒の浄化活性温度を低温化すること及び浄化効率を上げることが知られている (特開平 7-247827 号公報)。

50 【0003】また、還元触媒の硫黄による劣化の問題を解決しようとする技術としては、空燃比がリーンであるときに排気ガス中の  $\text{NO}_x$  を吸収し、空燃比がリッチであるときに吸収した  $\text{NO}_x$  を放出する  $\text{NO}_x$  吸蔵剤を使用した内燃機関の排気ガス浄化装置であって、 $\text{NO}_x$  吸蔵剤に吸収された硫黄吸収量が予め定められた所定量以

上となったことを判断する硫黄吸収量判断手段と、それによって所定量以上の硫黄が吸収されたと判断されるときに空燃比をリッチに設定するとともに、排気ガス浄化装置に流入する排気ガスの発熱量を増大する発熱量増大手段とを備えた内燃機関の排気ガス浄化装置の発明が開示されている。即ち、硫黄被毒した $\text{NO}_x$  吸蔵剤に対して、外部から電気ヒータなどにより加熱することなく硫黄を放出させるもので、排出ガスの発熱量を増大させるため、リーン失火手段により強制的に失火させ、出てきた炭化水素（HC）を触媒で燃焼させて排気ガス温度を上昇させ、また、点火時期を遅角制御させ、排気ガス温度を上昇させるものであることが開示されている（特開平10-54274号公報）。

#### 【0004】

【発明が解決しようとする課題】上記の内燃機関の排気管中にコロナ放電を発生させ、それにより排気ガス中の $\text{NO}_x$  を浄化する発明においては、還元剤としてHCを添加する炭化水素供給装置を還元触媒の入口に設置して、コロナ放電装置の上流には炭化水素を供給する装置は特に無い。図20は、HCが存在する場合と存在しない場合において、排気ガス温度と放電によりNOから $\text{NO}_2$  に酸化される量との関係を表わしたグラフである。ところで、コロナ放電でNOを $\text{NO}_2$  に酸化する場合には、HCが必要になる。これは、NOの酸化反応がちょうど光化学反応と同じ反応をするため、HCが存在しないガス中ではNOが $\text{NO}_2$  に酸化する反応はほとんど進まないからである。図20から明らかなように、コロナ放電下で、HC存在時においては、排気ガスが低温の時からNOの $\text{NO}_2$  への酸化が認められるが、HCが存在しない場合には酸化はほとんど認められない。上記の発明では、HCを添加する炭化水素供給装置をコロナ放電装置と還元触媒との間に設置しているため、コロナ放電装置にはHCが供給されない。そのため、ディーゼルエンジン等のような内燃機関において燃料が完全に燃焼した場合には、排気ガス中にはHCは存在せず、この結果、NOを $\text{NO}_2$  に酸化させることができない。また、 $\text{NO}_2$  還元時においてもコロナ放電でHCも分解、イオン化した方が浄化率が向上すると共に活性温度を下げるができるが、しかし、上記の発明では、HCはコロナ放電装置を通らないためHCの分解、イオン化をすることができず、放電による効果が得られないという問題がある。更に、還元剤としてのHCは内燃機関の筒内で添加することにより、部分酸化されて $\text{NO}_x$  浄化効率が上がることも知られているが、上記の発明では、この効果を利用することもできないという問題がある。

【0005】また、上記の内燃機関の排気浄化装置の発明は、排気ガス温度を上昇させて硫黄被毒触媒の温度を上昇させ、硫黄被毒を回復させるものであるが、 $\text{NO}_x$  吸蔵触媒の温度を硫黄被毒が回復可能なレベルまで上昇

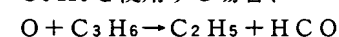
させるためには、多量のHCを必要とし、このため失火制御を多数回繰り返すことが必要で、内燃機関の運転状態が不安定になるという問題がある。また、遅角制御で排気ガス温度を上げる場合も、エンジンの運転バランスが崩れ、エンジン出力が変化して乗り心地が悪くなる。このように、運転状態が変化することで、車両を安定走行させることが難しいという問題がある。また、燃焼によって触媒温度を上げる場合、周りの排気管も緩める必要があることから温度上昇に時間がかかり、その間無駄な燃料を消費することになり、更に被毒回復後、通常の使用をする場合、触媒の持つ熱容量で今度は逆に温度が下がらず、その間 $\text{NO}_x$  浄化ができない状態となるという問題もある。以上の理由から、HCを燃焼させることで、触媒の温度を上げ硫黄被毒を回復させる方法には多くの問題があると言える。

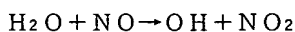
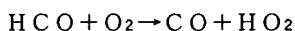
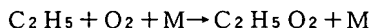
【0006】本発明は、上記の問題点を鑑みてなされたものであって、その目的とするところは、内燃機関から排出される排気ガス中の $\text{NO}_x$  除去を良好に行なおうとする際に、（1）還元剤含有排気ガス及び触媒を活性化し、NOの $\text{NO}_2$  への酸化、 $\text{NO}_2$  の $\text{N}_2$  への還元をより効果的に行う、（2） $\text{NO}_x$  吸蔵還元触媒、選択還元型 $\text{NO}_x$  触媒等の触媒（例えば、アルミナ、ゼオライト系の還元触媒）に硫黄被毒が生じるのを抑制・制御する、（3）発生した硫黄被毒触媒の劣化を回復する、（4）触媒への硫黄被毒の抑制・制御、発生した硫黄被毒触媒の劣化回復を、上記のような内燃機関の運転状態のバランスを崩すことがない状態でもできる、ような排気ガス処理装置を提供することである。

#### 【0007】

【課題を解決するための手段】本発明者らは、内燃機関から排出される排気ガス中の $\text{NO}_x$  除去を行なう際に使用する $\text{NO}_x$  吸蔵還元触媒及び選択還元型 $\text{NO}_x$  触媒（以下、単に「触媒」ということがある。）の還元剤存在下での触媒作用、その触媒作用とプラズマ放電との関係、触媒に硫黄被毒が生じる現象、そのことによる触媒の劣化、硫黄被毒触媒の回復等について調査・研究をしていたところ、次のようなことを見だし、本発明を完成したものである。

【0008】[NOの $\text{NO}_2$  への酸化について] ディーゼルエンジン等から排出される排気ガス中の窒素酸化物（ $\text{NO}_x$ ）にはNOが多いが、選択還元触媒の場合、NOよりも $\text{NO}_2$  の方が浄化率が高いこと（上記特開平7-247827号公報の図9、10を参照）。しかし、NOの $\text{NO}_2$  への酸化は、光化学反応と同様であるためにHCが必要であり、HCが存在しない環境下では、 $\text{NO}_2$  への酸化はプラズマ放電領域においてもほとんど進まないこと、即ち、プラズマ放電により、HCの存在下でのNOの $\text{NO}_2$  への酸化反応は、例えば、HCとして $\text{C}_3\text{H}_6$ を使用する場合、





のような反応が生じ、NOがNO<sub>2</sub>に酸化されること。したがって、NOがNO<sub>2</sub>になるためにはHCが必要であること（鈴木伸著、「大気科学」、東京大学出版1979、p. 37～40参照）。

【触媒活性について】HCがプラズマ放電領域を通ることによりイオン化もしくは分解され、プラズマと接触した触媒の活性が向上し、触媒反応が進みやすくなり、また、プラズマ放電により触媒と接触する排気ガスの温度も上昇するため、エンジンから排出される排気ガスの温度が低温域にある時から高いNO<sub>x</sub>浄化を得ることができ、NO<sub>x</sub>吸蔵還元触媒の場合、NOよりもNO<sub>2</sub>の方がより低温で触媒に吸蔵されること、排気ガスの温度が触媒で十分浄化できる温度ではプラズマ放電を発生しなくとも排気ガスの浄化率を高い状態に維持できること。

【0009】【触媒への硫黄被毒について】NO<sub>x</sub>吸蔵還元型触媒では、内燃機関から排出されたNO<sub>x</sub>を吸蔵する場合NOが触媒表面上で酸化されてNO<sub>2</sub>、NO<sub>3</sub>となって吸蔵されること、他方、SO<sub>2</sub>が触媒表面上に到達した場合には、SO<sub>2</sub>がSO<sub>3</sub>となってNO<sub>3</sub>の代わりに吸蔵されるが、通常の内燃機関運転領域である排気ガスが低温の状態（600℃以下）では、吸蔵されたSO<sub>3</sub>がなかなか還元されず、硫黄被毒として触媒の吸蔵能力を悪化させる原因になること、NO<sub>2</sub>とSO<sub>2</sub>の双方が触媒表面に到達した場合には、SO<sub>2</sub>と比較してNO<sub>2</sub>の方がより触媒に吸蔵されやすいこと、触媒あるいは触媒に対して排気ガス上流側で、適当な電圧で放電を発生させることにより、排気ガス中のNOを選択的にNO<sub>2</sub>に酸化させることができること、還元剤のHC成分をプラズマ放電により部分酸化、分解することで生成されるCO或いはH<sub>2</sub>によりSO<sub>3</sub>は、SO<sub>2</sub>として放出することができること、O<sub>2</sub>が存在しない雰囲気場においても、HCはラジカル化しSO<sub>3</sub>の還元反応を促進することができること、NO<sub>2</sub>はSO<sub>2</sub>と比較して素早く触媒に吸蔵される性質があるため、硫黄被毒が生じる前に吸蔵され、硫黄被毒がされにくくなること、結果として、硫黄が含まれた燃料を使用しても、硫黄被毒がしにくい状態とすることができること。

【0010】【対策手段について】

・NOのNO<sub>2</sub>への酸化に対して、内燃機関の筒内あるいは排気管にHCを添加せず、HCが無い状態では、プラズマ放電によってもNOがNO<sub>2</sub>に酸化されにくいいため、筒内もしくは排気管内のプラズマ放電領域よりも排気ガス上流側に、還元剤（HC）を添加する還元剤添加装置を設け、HCを添加することが必要であること。

・触媒活性について、内燃機関の状態に応じて（排気ガス温度の高低などに応じて）プラズマ放電の発生状態を制御することが必要であること。

・触媒への硫黄被毒の抑制・制御に対して、触媒が被毒し易い排気ガス雰囲気にあるかどうかを判定（検出もしくは推定）し、被毒回避のための放電を発生させるべきか否かの制御をする易被毒劣化状態判定・制御手段を設けることが必要であること。

・硫黄被毒触媒の劣化回復に対して、触媒の被毒劣化状態を判定（検出もしくは推定）し、被毒回復のための放電を発生させるべきか否かの制御をする被毒劣化状態判定・制御手段を設けることが必要であること。以上のような現象及び対策手段を見いだすことにより本発明を完成したものである。

【0011】即ち、本発明に係る排気ガス浄化装置は、「内燃機関からの排気ガスを浄化する装置であって、内燃機関の排気管に設けた触媒と、該触媒又は該触媒に対して排気ガス上流側の少なくとも一方で放電を発生させる放電装置と、該放電装置に電圧をかける高電圧電源と、内燃機関の筒内又は放電発生領域よりも排気ガス上流側の排気管中の少なくとも一方で還元剤を添加する還元剤添加装置とを有することを特徴とする触媒の活性向上機能を有する排気ガス浄化装置。」（請求項1）を要旨（発明を特定する事項）とする。また、本発明に係る排気ガス浄化装置は、

・排気ガス温度を計測するガス温度計と、該温度計からの計測温度に基づいて放電電圧、還元剤量を制御する制御装置を有すること（請求項2）、

・内燃機関の回転数、負荷、吸入空気量、主噴射燃料量などの運転状態に係る情報を検出するセンサーと、該センサーからの信号を基に内燃機関を制御する制御装置と、内燃機関の運転状況に基づいて放電電圧、還元剤量を制御する制御装置とを有すること（請求項3）、

・内燃機関から排出される排気ガス中の炭化水素量を検出するセンサーを放電領域よりも排気ガス上流側に有すること（請求項4）、

・上記放電装置が、触媒の排気ガス上流側に設けた電極間に誘電体を挟んだものであること（請求項9）、

・上記放電装置が、導電性金属から構成された排気管ケースと該排気管ケース内面に密接して設けられた筒状の絶縁物と、該絶縁物に密接して設けられた複数の板状の電極とからなり、該電極の円周方向の長さ（m）と該電極間の円周方向の長さ（n）との比が、 $m/n = 1/1 \sim 1/10$ であること（請求項10）、の少なくとも一つを、発明を特定する事項とすることができる。

【0012】また、本発明に係る排気ガス浄化装置は、「内燃機関からの排気ガスを浄化する装置であって、内燃機関の排気管に設けた触媒と、該触媒又は該触媒に対して排気ガス上流側の少なくとも一方で放電を発生させることで排気ガスの温度を上昇させる効果、排気ガスを

活性化させる効果、触媒の温度を上昇させる効果、触媒の活性を向上させる効果のうちの1つ以上の効果により触媒の被毒劣化を抑制せしめる放電装置と、該放電装置に電圧をかける高電圧電源と、触媒が被毒劣化し易い状態か否かを判定し、高電圧電源を制御する易被毒劣化状態判定・制御手段とを有することを特徴とする触媒被毒劣化抑制機能を有する排気ガス浄化装置。」(請求項5)を要旨(発明を特定する事項)とする。また、本発明に係る排気ガス浄化装置は、

- ・内燃機関の運転状態をコントロールする内燃機関制御装置を有すること、
- ・内燃機関の筒内又は放電発生領域よりも排気ガス上流側の排気管中の少なくとも一方で還元剤を添加する還元剤添加装置を有すること(請求項8)、
- ・上記放電装置が、触媒の排気ガス上流側に設けた電極間に誘電体を挟んだものであること(請求項9)、
- ・上記放電装置が、導電性金属から構成された排気管ケースと該排気管ケース内面に密接して設けられた筒状の絶縁物と、該絶縁物に密接して設けられた複数の板状の電極とからなり、該電極の円周方向の長さ(m)と該電極間の円周方向の長さ(n)との比が、 $m/n = 1/1 \sim 1/10$ であること(請求項10)、の少なくとも一つを、発明を特定する事項とすることができる。

【0013】また、本発明に係る排気ガス浄化装置は、「内燃機関からの排気ガスを浄化する装置であって、内燃機関の排気管に設けた触媒と、該触媒又は該触媒に対して排気ガス上流側の少なくとも一方で放電を発生させることで排気ガスの温度を上昇させる効果、排気ガスを活性化させる効果、触媒の温度を上昇させる効果、触媒の活性を向上させる効果のうちの1つ以上の効果により硫黄被毒触媒の被毒劣化を回復せしめる放電装置と、該放電装置に電圧をかける高電圧電源と、触媒が被毒劣化された状態を判定し、高電圧電源を制御する被毒劣化状態判定・制御手段とを有することを特徴とする触媒被毒劣化回復機能を有する排気ガス浄化装置。」(請求項6)を要旨(発明を特定する事項)とする。また、本発明に係る排気ガス浄化装置は、

- ・内燃機関の運転状態をコントロールする内燃機関制御装置を有すること、
- ・内燃機関の筒内又は放電発生領域よりも排気ガス上流側の排気管中の少なくとも一方で還元剤を添加する還元剤添加装置を有すること(請求項8)、
- ・上記放電装置が、触媒の排気ガス上流側に設けた電極間に誘電体を挟んだものであること(請求項9)、
- ・上記放電装置が、導電性金属から構成された排気管ケースと該排気管ケース内面に密接して設けられた筒状の絶縁物と、該絶縁物に密接して設けられた複数の板状の電極とからなり、該電極の円周方向の長さ(m)と該電極間の円周方向の長さ(n)との比が、 $m/n = 1/1 \sim 1/10$ であること(請求項10)、の少なくとも

一つを、発明を特定する事項とすることができる。

【0014】また、本発明に係る排気ガス浄化装置は、「内燃機関からの排気ガスを浄化する装置であって、内燃機関の排気管に設けた触媒と、該触媒又は該触媒に対して排気ガス上流側の少なくとも一方で放電を発生させることで排気ガスの温度を上昇させる効果、排気ガスを活性化させる効果、触媒の温度を上昇させる効果、触媒の活性を向上させる効果のうちの1つ以上の効果により触媒の被毒劣化を抑制・回復せしめる放電装置と、該放電装置に電圧をかける高電圧電源と、触媒が被毒劣化し易い状態か否かまたは触媒が被毒劣化した状態かを判定し、高電圧電源を制御する被毒劣化状態判定・制御手段とを有することを特徴とする触媒被毒劣化抑制・回復機能を有する排気ガス浄化装置。」(請求項7)を要旨(発明を特定する事項)とする。また、本発明に係る排気ガス浄化装置は、

- ・内燃機関の運転状態をコントロールする内燃機関制御装置を有すること、
- ・内燃機関の筒内又は放電発生領域よりも排気ガス上流側の排気管中の少なくとも一方で還元剤を添加する還元剤添加装置を有すること(請求項8)、
- ・上記放電装置が、触媒の排気ガス上流側に設けた電極間に誘電体を挟んだものであること(請求項9)、
- ・上記放電装置が、導電性金属から構成された排気管ケースと該排気管ケース内面に密接して設けられた筒状の絶縁物と、該絶縁物に密接して設けられた複数の板状の電極とからなり、該電極の円周方向の長さ(m)と該電極間の円周方向の長さ(n)との比が、 $m/n = 1/1 \sim 1/10$ であること(請求項10)、の少なくとも一つを、発明を特定する事項とすることができる。

#### 【0015】

【発明の実施の形態】本発明は、内燃機関からの排気ガスを浄化する装置において、(1)筒内または排気管内のプラズマ放電領域よりも排気ガス上流側(以下、単に「上流側」という)に、還元剤(HC)を添加する還元剤添加装置を設けること、(2)内燃機関の状態に応じてプラズマ放電の発生状態を制御すること、(3)触媒が被毒しやすい排気ガス雰囲気にあるかどうかを判定(検出または推定)し、被毒回避のための放電を発生させるべきか否かを判定・制御する易被毒劣化状態判定・制御手段を設けること、(4)触媒の被毒劣化状態を判定(検出又は推定)し、被毒回復のための放電を発生させるべきか否かを判定・制御する被毒劣化状態判定・制御手段等を設けること、を特徴とするものである。

【0016】以下において、本発明の実施の形態を図面を参照して、詳細に説明するが、本発明は、以下の実施の形態によって限定されるものではない。図1は、本発明に係る内燃機関の排気ガス浄化装置の第1の実施形態の概略図である。即ち、触媒活性機能を有する排気ガス浄化装置の概略図である。該内燃機関の排気ガス浄化装

置は、ディーゼルエンジン等の内燃機関1の排気管2に設けられた排気管ケース2'、排気管ケース2'内に上流側から順次配置された放電装置7と触媒3、放電装置7の電極間にパルス状の高電圧を供給するパルス高電圧発生装置5、排気管ケース2'の上流側及び下流側に設けられた排気ガスの温度を計測するための温度計81、82、内燃機関1の運転状態をコントロールする内燃機関制御装置91、内燃機関制御装置91に制御に必要な情報を計測するセンサー9、放電装置7の放電を開始するか否かを決定、パルス高電圧発生装置5を制御する第2内燃機関制御装置92、排気ガスを浄化するために必要な還元剤を排気管2の放電発生領域よりも上流側に添加する還元剤添加装置10とから構成されている。内燃機関制御装置91は、センサー9で計測されたアクセル量、エンジン回転数、冷却水温などの信号をもとに、内燃機関1の運転状態を制御する。排気ガス温度を直接計測する代わりに内燃機関の運転状態から推定してもよい。その場合には、温度計81を省略することができる。また、温度計82により触媒後方(触媒出口)からの排出ガス温度を計測する代わりに触媒3の中の温度を計測してもよい。また、還元剤を排気管2の放電発生領域よりも上流側に添加する還元剤添加装置10の代わりに、筒内に還元剤(HC)を添加する装置でもよい。いずれの場合も、放電発生領域よりも上流側でHCが添加されるために、放電領域においては必要なHCが供給され、また、排気ガス温度が高温である場においてHCが添加されることになり、HCは容易に気化し、排気ガス中に均一に混ざりになる。更に、放電を触媒3の上流側で発生させる代わりに触媒3中で発生させてもよく、この場合には、触媒表面での反応が促進され、より浄化活性を上げることができるし、排気ガス低温でのNO<sub>2</sub>の触媒への吸蔵による効果と触媒表面での反応の活性効果との相乗効果により高いNO<sub>x</sub>浄化率が得られる。

【0017】図2は、放電装置7の具体的な構成の一例を示す図であり、図3は、図2のX、X切断断面図である。101は、排気管ケースで導電性の金属で構成されており、接地されていて陰極となる。102は、排気管ケース101内に設けられた絶縁物で、セラミック又は石英等で作られていて、金属の排気管ケース101と密接している。103は、導電性の陽極電極で、絶縁物102の内側に密接して設けられる。電極の円周方向の長さ(m)と電極間の円周方向の長さ(n)との比は、 $m/n = 1/1 \sim 1/10$ の間の適当な値に設定されている。電極103には、プラグ105より導線が繋がれており、パルス高電圧発生装置5より高電圧が供給される。104は、スペーサーで、排気ガスが電極の近傍を通過するように中央部に設置されている。スペーサー104は、碍子106により排気管ケース101に固定されていて、排気管ケース101、陽極電極103とは絶

縁状態にある。

【0018】次に、上記内燃機関の排気ガス浄化装置による排気ガスの浄化について、図面を参照して詳細に説明する。図4は、排気ガス温度と窒素酸化物の発生量(TNO<sub>x</sub>)と当量比との関係を表わしたグラフであり、図5は、エンジン回転数と噴射燃料量と等未燃HC濃度線との関係を表わしたグラフであり、図6は、排気ガス温度と窒素酸化物の発生量(TNO<sub>x</sub>)との関係を表わしたグラフであり、図7は、窒素酸化物の発生量と放電装置に印加するパルス電圧との関係を表わした図である。

【0019】[還元剤添加量の制御] センサー9で計測したエンジン回転数、吸入空気量、負荷と燃料量が第1内燃機関制御装置91の信号として第2内燃機関制御装置92に伝達される。第2内燃機関制御装置92では、吸入空気量と燃料量とから当量比を算出し、得られた当量比と温度計81で計測した排気ガス温度とから図4に示すマップにより、窒素酸化物の発生量(TNO<sub>x</sub>)を求める。また、第2内燃機関制御装置92では、エンジン回転数と燃料量から図5に示すマップを用いて未燃HC量(THCmap)を算出し、冷却水温(Tw)による補正を次式で加え、補正した未燃HC量(THC)を求める。

$THC = THC_{map} - a \cdot Tw + b$  (a, b は定数)

次に、第2内燃機関制御装置92では、TNO<sub>x</sub>とTHCから、次式で還元剤添加装置から添加するHC量(AHC)を算出し、添加するHC量を制御する。

$AHC = a \cdot TNO_x - THC$  (a は定数)

なお、排気管内の未燃HC量は、回転数、燃料噴射量、冷却水温から推定したが、放電装置と内燃機関との間の排気管中にNO<sub>x</sub>センサーやHCセンサーを取付、直接測定してもよい。また、HC(THCmap)量は、排気管中にセンサーを設け、直接測定してもよい。還元剤添加装置から添加するHC量(AHC)は、排気ガス温度を計測するガス温度計からの計測温度に基づいて制御することもできる。即ち、排気ガス温度が高温になり、触媒のみで排気ガス浄化が進む温度域では、放電を中止し、還元剤量も触媒による排気ガス浄化に必要な量のみ制限する。このような時には、排気ガス温度を計測するガス温度計からの計測温度にのみ基づいて制御することができる。

【0020】[放電電圧の制御] 触媒出口の排気ガス温度が温度計82で計測され、第2内燃機関制御装置92では、上記のようにして得られた窒素酸化物の発生量(TNO<sub>x</sub>)と温度計82で計測された排気ガス温度とから放電を発生させるか否かを判定する。即ち、TNO<sub>x</sub>及び温度計82で計測された排気ガスの温度が、図6における(i)の領域(この領域は、触媒温度が低温で触媒3の効果が少なく排気ガス中のNO<sub>x</sub>量が多い領域

である)に入っている場合は、排気ガスに放電を施し、NOをNO<sub>2</sub>に酸化させるとともに還元剤も分解、イオン化させる。この放電により、NO<sub>x</sub>をNO<sub>2</sub>として触媒3に吸着させるとともに反応温度を低温側にシフトさせ、排出されるNO<sub>x</sub>量を低減することができる。また、TNO<sub>x</sub>及び温度計82で計測した排気ガス温度が、図6における(i i)の領域(この領域は、NO<sub>x</sub>量が少ないか又は触媒温度が高い状態なので、触媒活性が得られる領域である)に入っている場合は、放電をやめ浄化を触媒の能力にまかせる。これにより、放電エネルギーを節約することができる。第2内燃機関制御装置92では、上記の放電を発生させるか否かの判断をするとともに図7にしたがってパルス高電圧発生装置5より放電装置7に供給するパルス電圧を決定し、その信号をパルス高電圧発生装置5に送る。信号を受け取ったパルス高電圧発生装置5では、その信号に応じてパルス電圧を放電装置7に供給する。放電装置7では、高電圧が図2で示した電極にかけられると図3中のnの部分にプラズマが発生する。プラズマを効率良く発生させるためには、電極の円周方向の長さ(m)と電極間の円周方向の長さ(n)との関係が重要で、これは課題とするシステム(本発明が適用されるNO<sub>x</sub>浄化システム)で変更する必要がある。図面に示されている例では、その比は、 $m/n=1/1$ である。なお、陰極電極101と陽極電極103は、絶縁体102に密着している方が効率良くプラズマを発生することができる。また、上記のような放電電圧の制御を、センサー9で計測したエンジン回転数、吸入空気量、負荷、燃料量等の内燃機関に係る情報と排出ガス温度を計測した温度計81、82等からの信号との両方の信号に基づいて行なう代わりに、排気ガス温度が高温になり、触媒のみで排気ガス浄化が進む温度域では、排出ガス温度を計測した温度計81、82等からの信号のみに基づいて行なってもよい。

【0021】図8は、本発明と従来技術(放電装置が無い排気ガス浄化装置)について、排気ガス温度に対する触媒出口でのNO<sub>x</sub>量を示したグラフである。このグラフは、内燃機関の負荷を徐々に上げ、内燃機関からの排気ガス温度が徐々に上昇していった場合の触媒出口でのNO<sub>x</sub>量をプロットしたものである。図8から、触媒のみを使う従来技術では、排気ガスが低温の領域(図8中Bの領域)ではNO<sub>x</sub>浄化はほとんど進まないこと、排気ガス温度が上昇するにつれて、触媒の活性が現れる様になり、Dの領域になると十分な浄化が始まること、このため、低温域ではほとんどNO<sub>x</sub>の浄化がされないことが明らかである。他方、本発明においては、触媒活性がない排気ガス低温のBの領域では、NOがNO<sub>2</sub>にされることで、触媒および配管中に吸着され(低温時には、燃焼ガスの水分が配管内部に付くため、これに吸着される)、触媒出口からの排出が抑制されること、排気ガス温度の上昇とともに触媒温度が上昇してくると触

媒の活性が働き始めるが、HCが放電により部分分解、イオン化されることで、放電がない場合と比較して排気ガスが低温のときから触媒活性が生じていることが明らかである。また、図8中のBの領域では、放電がない従来技術においては触媒活性が十分得られていないが、本発明においては放電装置によって触媒活性が得られていること、A点より高温の温度においては、放電装置を作動させなくとも触媒の十分な活性が得られるため、従来技術におけると同じ浄化特性が得られていることが明らかである。このように、本発明によれば、常に変化する排気ガス温度に対しても常に高い浄化率を提供することが可能になる。なお、放電により排気ガスの浄化を行う場合、その排気ガスの温度、組成、流量(放電中の滞在時間)に対応した適切な電流、電圧が存在する。そのため、エンジンの運転状態の信号からその時の排気ガス温度、組成、流量を推察したり、また、直接排気管中で測定することにより、その時の排気ガス状態に最も適した電圧、電流をかけるよう制御することも可能である。このような制御により、消費電力を抑えて効率良く排気ガスの浄化をすることができる。

【0022】図9は、本発明に係る内燃機関の排気ガス浄化装置の第2の実施形態の概略図である。即ち、被毒抑制機能を有する内燃機関の排気ガス浄化装置の概略図を示すものである。図10は、本発明に係る内燃機関の排気ガス浄化装置の第2の実施形態の電極部分の他の構造を示したものである。該内燃機関の排気ガス浄化装置は、内燃機関1の排気管2に設けられた触媒3、触媒3の上流側に設けられた通気性を有する円盤状の一对の電極42、43、一对の電極42、43間にパルス状の高電圧を供給するパルス高電圧発生装置5、内燃機関1の運転状態をコントロールする内燃機関制御装置91、内燃機関制御装置91に制御に必要な情報を計測するセンサー9、触媒3が被毒され易い状態にあるか否かを判定(検出又は推定)し、パルス高電圧発生装置5を制御する易被毒劣化状態判定・制御手段93、易被毒劣化状態判定・制御手段93が判断するための材料として用いる、一对の電極42、43と触媒3よりも上流側的气体温度と、触媒を通過した後の排気ガス温度とを計測する温度計81、82とから構成されている。なお、一对の電極42、43間に放電(プラズマ)が生じやすいように誘電体41(例えば、アルミナ)を挟むこともできる。また、上記の装置では、触媒3の上流側に設けられた通気性を有する円盤状の一对の電極42、43の代わりに、図10に示されているように、触媒3の上流側に設けられた棒状の電極44と、その電極44と対応した位置で、排気管2の外周に筒状の電極45とを設けてもよい。また、上記の装置では、内燃機関の筒内あるいは排気管に還元剤(HC)を添加する還元剤添加装置を設けていないが、HCが無い状態では、放電によりNOがNO<sub>2</sub>に酸化されにくいために、筒内へのHC添加もし

くは排気管内へのHC添加を行う還元剤添加装置を設けることも可能である。

【0023】次に、上記内燃機関の排気ガス浄化装置による排気ガスの浄化について、図面を参照して詳細に説明する。図11は、触媒前後における排気ガスの平均温度と排気ガス中の硫黄の量との関係を表わした図である。内燃機関制御コンピューター91は、センサー9で計測されたアクセル量、エンジン回転数、冷却水温等の信号をもとに、内燃機関1の運転状態を制御する。同時に噴射燃料量、エンジン回転数、EGR量からの排気ガス量を易被毒劣化状態判定手段93に伝達する。更に、易被毒劣化状態判定手段93には、触媒前後に設けた温度計81、82からの信号が入力される。易被毒劣化状態判定手段93では、噴射された燃料と吸入空気量から、排気ガス中の硫黄濃度を推定する。燃料に含まれている硫黄量はほぼ一定であるため、燃料量から硫黄量（イオウ濃度）は推定できる。更に、温度計81、82の平均温度を求める。そして、図11で示したグラフにおいて領域Cに入った場合、易被毒劣化状態判定手段93が、触媒が被毒されやすい状態であると判定して放電発生信号をパルス高電圧発生装置5に送る。パルス高電圧発生装置5は、信号を受け取ると高電圧パルスを生じ、電極42、43を介して排気ガスに高電圧パルスをかけて放電を生じさせる。ここでは、高電圧を、より効果が高い高電圧パルスとして発生させるパルス高電圧発生装置を用いたが、定圧の高電圧発生装置でも構わない。

【0024】図12は、本発明と従来技術（硫黄被毒の抑制装置を用いない方法）について、使用時間に対する触媒のNOxの吸収能力（吸蔵可能量）を示したグラフである。図12は、触媒内のNOxを一度還元したときのNOx吸蔵量の変化（再生処理された後の触媒のNOx吸蔵量の変化）を、使用時間に対して示したものである。本発明では、より長時間に渡ってNOx吸収能力があるのに対して、従来技術では、すぐ硫黄に被毒され吸収できなくなることが分かる。図12から、本発明では、触媒としての劣化時期を大幅に改善できることが明らかである。このことは、NOx吸蔵還元触媒では、内燃機関から排出されたNOは触媒表面上で酸化されNO<sub>2</sub>、NO<sub>3</sub>となって吸蔵されるが、他方、一般にはSO<sub>2</sub>がSO<sub>3</sub>となってNO<sub>3</sub>の代わりに吸蔵されるものと考えられる。また、放電では、SO<sub>2</sub>の酸化（SO<sub>2</sub>→SO<sub>3</sub>）よりもNOの酸化（NO→NO<sub>2</sub>）の方が進み\*

$$Lrich = f(rpm, Gegr, Fuel) - (1)$$

【0027】図15は、排気ガス温度と触媒に硫黄が吸蔵され易い状態との関係を表わしたグラフである。リーン雰囲気における吸蔵還元触媒のイオウ吸蔵は、ある温度域で盛んになり、排気ガス低温側では少ない。また、排気ガス高温域では触媒内に入ったイオウは吸蔵される前に触媒外へ出てしまう上、吸蔵されていたイオウも放

\*やすい。この時、NO<sub>2</sub>が触媒に到達した場合には、SO<sub>2</sub>と比較してNO<sub>2</sub>の方がより触媒に吸蔵されやすく、そこで、本発明においては、放電によって、排気ガス中のNOのみがNO<sub>2</sub>に酸化され、触媒に到達するために、SO<sub>2</sub>と比較してNO<sub>2</sub>の方が触媒に吸蔵され、その結果、硫黄被毒がされにくくなるものと考えられる。

【0025】図13は、本発明に係る内燃機関の排気ガス浄化装置の第3の実施形態の概略図を示す図である。即ち、被毒回復機能を有する内燃機関の排気ガス浄化装置の概略図を示すものである。該内燃機関の排気ガス浄化装置は、内燃機関1、排気管2に設けられた触媒3、触媒3を挟む形で設けられ、触媒3に高電圧をかける電極4、4にパルス状の高電圧を供給するパルス高電圧発生装置5、内燃機関1の運転状態をコントロールする内燃機関制御装置91、内燃機関制御装置91に制御に必要な情報を計測するセンサー9、触媒3の被毒劣化状態を判定（検出又は推定）し、パルス高電圧発生装置5を制御する被毒劣化状態判定・制御手段94、被毒劣化状態判定・制御手段94が被毒劣化状態を判断するための情報として用いる触媒入り口のガス温度を計測する温度計8、被毒劣化触媒を回復させるために必要な還元剤を内燃機関1の筒内に添加する還元剤添加装置10とから構成されている。なお、還元剤添加装置10の代わりに内燃機関1の制御により、添加剤を筒内に添加する形をとってもよい。また、筒内ではなく内燃機関出口の排気管2内で、触媒よりも上流側に還元剤を添加する還元剤添加装置10を設けてもよい。

【0026】次に、硫黄の回復制御について詳細に説明する。図14は、イオウ被毒の判定フローチャートを示すものである。内燃機関1としてディーゼルエンジンを、排気ガス中の有害成分を除去するための触媒3としてNOx吸蔵還元触媒をもちいる場合、NOx吸蔵還元触媒が燃料中に含まれる硫黄によって被毒され性能が劣化することがある。触媒のイオウ劣化は、触媒を通過した排気ガス中のイオウの量とその時の排気ガスの温度、及び排気ガスの当量比から決まる。被毒劣化状態判定・制御手段94は、最初に、内燃機関制御装置91からエンジンの回転数、EGR量、噴射燃料量を得る。エンジン回転数（rpm）とEGR量（Gegr）から吸入空気量（GA）を算出し、噴射燃料量（fuel）とから排出ガスがリッチ状態にあるのか、リーン状態にあるのかを判定する。この値をLrichとする。

出される。低温域では、イオウの吸蔵反応が進まないため、吸蔵される量は少ない。以上の結果をまとめ、イオウが被毒吸蔵され易い状態を+（プラス）で、吸蔵されず放出される方を-（マイナス）で表し、触媒への排気ガス温度を横軸としてグラフを書くことにより、図15を得る。次に温度計8で計測される排気ガス温度（Tg



a s) を使って、図15より係数Cを求める。

【0028】図16は、排気ガス流量と触媒への硫黄の吸蔵、離脱の関係を表わす係数Bを、排気ガス流量との関係で表わしたグラフである。吸蔵還元触媒の場合、リッチ雰囲気でイオウが吸蔵される大きさは小さいため、イオウの吸蔵量が増加することはほとんどない。また、吸蔵還元触媒が吸蔵するイオウの量は、その排気ガス流量および、排気ガス中のイオウの濃度に影響される。排気ガス流量(GA)については、エンジン回転数とEGR量から算出することができ、また、排気ガス中のイオウの濃度(S)は噴射された燃焼量(fuel)から算出することができる。これらを式で表わすと、

$$GA = f(rpm, Gegr) - (2)$$

$$S = f(fuel) - (3)$$

と表すことができる。当然のことながら、同じ排気ガスの温度、流量であっても排気ガス中のイオウ量が多いと吸蔵される量は多くなり、また、高温時に脱離するイオウ量も少なくなる。また、図16に示すように、排気ガス流量が小さい時ほど吸蔵還元触媒へのイオウの吸蔵量が増え、排気ガス流量が大きい場合には、吸蔵還元触媒へのイオウの吸蔵、脱離できる量が減る。図16を用いてこの関係を表す係数Bを求める。

【0029】図17は、内燃機関の運転時間と触媒への吸蔵硫黄量の積算値との関係を表わしたグラフである。\*

$$Stot(t) = Stot(t-1) + \Delta S - (5)$$

ここで、tは、時間を表わす。積算値 $Stot(t)$ は、内燃機関の未運転時は0に設定されている値で、内燃機関が運転はじめると(5)式により加減算されていく。

・ステップ7(S7)：別に定めた閾値A(これ以上硫黄が着かなくなった状態を100とした場合に、例えば、80となったときの値をしきい値Aとする)を $Stot(t)$ が超えているか否かを判定する。 $Stot(t)$ が閾値Aを超えている場合には、触媒がイオウ被毒した状態ということで劣化回復処理をする。 $Stot(t)$ が閾値Aよりも小さい場合には、まだ劣化状態ではないということで、この判定ループを終了する。この判定ループは、内燃機関が動作中、一定間隔で、搭載したコンピュータにより計算され、 $Stot(t)$ が計算される。

【0030】硫黄被毒劣化状態であると判定された場合には、以下のような劣化回復処理が施される。即ち、上記の判定ループに示されているように、被毒劣化状態判定・制御手段94で触媒3が被毒劣化されていると判定されると、その信号は先ずパルス高電圧発生装置5に伝えられる。パルス高電圧発生装置5では、触媒3に放電を与えるに必要な高電圧が発生する。この電圧は一定電圧でも良いがパルス状の電圧の方が被毒回復効果が大きい。パルス高電圧発生装置5で発生したパルス高電圧は電極4より触媒3にかけられる。他方、被毒劣化の判定

\*次に、図14のフローチャートを参照して、吸蔵還元触媒へのイオウ被毒の判定ループについて説明する。スタートから終了までの各ステップ(ステップ1～ステップ7)での処理は以下の通りである。

・ステップ1(S1)：エンジン回転数(rpm)，EGR量(Gegr)，噴射燃料量(fuel)，排気ガス温度(Tgas)の測定、排気ガス流量(GA)，排気ガス中のイオウの濃度(S)の算出。

・ステップ2(S2)：ステップ1で計測したデータを基に(1)式からLrichを求め、排気ガスがリッチか否かを判定。

・ステップ3(S3)：ステップ2でリッチと判定された場合、温度計8で測定した温度を基に図15から係数Cを求める。ステップ2でリッチと判定された場合には、判定ループを終了する。

・ステップ4(S4)：式(2)を使って排気ガス流量(GA)を求め、図16から係数Bを求める。

・ステップ5(S5)：(3)式で求めたイオウ濃度(S)とステップ3，ステップ4で求めたB，Cを基にして、下記の推定式により、吸蔵イオウ量を推定する。

$$\Delta S = a * B * (C + S) - (4)$$

ここで、aは定数である。

・ステップ6(S6)：(4)式で得た $\Delta S$ を積算する。

信号は、内燃機関制御装置91にも伝達される。内燃機関制御装置91では、排気ガス成分が被毒回復に好都合な条件になるように運転状態を変化させる。NOx吸蔵還元触媒3の硫黄被毒の場合、酸素過剰雰囲気よりも還元雰囲気の方がより被毒回復が進む。このために、内燃機関制御装置91は、排気ガスが還元雰囲気になるように運転状態を制御する。また、還元剤添加装置10より、内燃機関筒内に還元剤(ここではHC)を添加することもできる。

【0031】この劣化処理の期間は、

$$T = b * Stot(t)$$

で表されるT時間だけ実行される。ここで、bは定数である。T時間後、劣化回復処理は終了し、 $Stot(t)$ には0が入る。ここで、劣化回復処理をしても、触媒の使用時間が長くなると十分回復できなくなる。そこで、劣化回復後に $Stot(t)$ に0を入れるのではなく、内燃機関の運転時間を測定し、

$$Stot(t)' = f(t)$$

とした関数で得られる値を劣化回復処理後に入れることも可能である。ここで、tは、触媒使用時間である。この方法により、触媒の回復後の能力をより正確に扱うことができる。

【0032】図18は、本発明に係る内燃機関の排気ガス浄化装置によって硫黄被毒を回復させた場合のNOx吸蔵量の変化を表わすグラフである。図18から明らか

なように、触媒の使用時間と共に $\text{NO}_x$ を吸蔵できる量が減ってくる。あるレベルを過ぎると、触媒の劣化判定がくだされ、劣化回復操作に入る（図18中のA、B）。放電による被毒劣化回復操作では、還元剤をイオン化することで活性を上げることができ、また、被毒した触媒表面のみを高温にできることで非常に短時間で被毒前の状態にまで回復させることができる。そして、被毒前の状態とほぼ等しい $\text{NO}_x$ 吸蔵量を持つ性能が得られる。他方、図18から明らかなように、触媒の温度を上げることのみで被毒劣化を回復させる従来の技術では、触媒全体が回復可能温度に達するまでに時間がかかる上、通常の内燃機関の運転領域では100%回復できない。したがって、図18に示したように、触媒の温度を上げることのみによる被毒劣化回復処理では、触媒の $\text{NO}_x$ 吸蔵量が回復処理を重ねるにしたがって徐々に少なくなるばかりでなく、被毒劣化回復に要する時間も多くなるといった問題もある。これに対して、放電を用いた本発明の装置による被毒劣化回復処理では、このような問題はなく、短時間で元の吸蔵量まで回復させることができるという優れた効果が奏されるのである。

【0033】図19は、被毒劣化回復に必要な排気ガス温度とそのときの回復量との関係を表わしたグラフである。図19においては、回復量が大きいほど、被毒劣化が良く回復していることを示している。放電を用いた本発明の装置では、放電で触媒の被毒面近傍で還元剤をイオン化し、活性能力を上げることができ、触媒表面近傍を局部的に高温にできるため、全体のガス温度から見ると低温域から高い回復量を得ることができる。他方、従来の触媒の温度を上げることのみによる硫黄被毒劣化回復技術では、完全に被毒劣化を回復させるためには排気ガス温度を高温にする必要があり、その排気ガス温度以下で回復処理をしても完全に元の状態には戻らない。そのため、内燃機関の種類によっては完全に回復させるに足る排気ガス温度を得ることが難しいものもあり、そのような内燃機関に設けられた触媒の場合には、触媒は徐々にその吸着能力を落としてしまうことになる。

#### 【0034】

【発明の効果】本発明は、以上詳記したとおり、

- ・内燃機関、特に、ディーゼルエンジンからの排気ガス中に含まれる窒素酸化物を効率的に浄化できる、
- ・通常では触媒活性が十分でない排気ガス低温域から浄化をすることができる、
- ・通常でも触媒活性が十分発揮できる排気ガス温度域では放電をやめ、触媒のみで浄化することにより、エネルギーの損失を抑えることができる、
- ・触媒の硫黄被毒が生じないようにして排ガス処理を行なうことができ、触媒としての劣化時期を大幅に改善することができる、
- ・触媒の硫黄被毒に対して、通常の加熱方法よりも低温

域において回復させることができると共に、短時間での回復、被毒前の状態への回復が可能になる、等の優れた効果を奏する。

#### 【図面の簡単な説明】

【図1】本発明に係る内燃機関の排気ガス浄化装置の第1の実施形態の概略図である。

【図2】放電装置7の具体的な構成の一例を示す図である。

【図3】図2のX、X切断断面図である。

10 【図4】排気ガス温度と窒素酸化物の発生量（ $\text{TNO}_x$ ）と当量比との関係を表わしたグラフである。

【図5】エンジン回転数と噴射燃料量と等未燃HC濃度線との関係を表わしたグラフである。

【図6】排気ガス温度と窒素酸化物の発生量（ $\text{TNO}_x$ ）との関係を表わしたグラフである。

【図7】窒素酸化物の発生量と放電装置に印加するパルス電圧との関係を表わした図である。

【図8】本発明と従来技術について、排気ガス温度に対する触媒出口での $\text{NO}_x$ 量を示したグラフである。

20 【図9】本発明に係る内燃機関の排気ガス浄化装置の第2の実施形態の概略図である。

【図10】本発明に係る内燃機関の排気ガス浄化装置の第2の実施形態の電極部分の他の構造を示したものである。

【図11】触媒前後における排気ガスの平均温度と排気ガス中の硫黄の量との関係を表わした図である。

【図12】本発明と従来技術について、使用時間に対する触媒の $\text{NO}_x$ の吸収能力を示したグラフである。

30 【図13】本発明に係る内燃機関の排気ガス浄化装置の第3の実施形態の概略図を示す図である。

【図14】イオウ被毒の判定フローチャートを示すものである。

【図15】排気ガス温度と触媒に硫黄が吸蔵され易い状態との関係を表わしたグラフである。

【図16】排気ガス流量と触媒への硫黄の吸蔵、離脱の関係を表わす係数Bを、排気ガス流量との関係で表わしたグラフである。

【図17】内燃機関の運転時間と触媒への吸蔵硫黄量の積算値との関係を表わしたグラフである。

40 【図18】本発明に係る内燃機関の排気ガス浄化装置によって硫黄被毒を回復させた場合の $\text{NO}_x$ 吸蔵量の変化を表わすグラフである。

【図19】被毒劣化回復に必要な排気ガス温度とそのときの回復量との関係を表わしたグラフである。

【図20】HCが存在する場合と存在しない場合において、排気ガス温度と放電によりNOから $\text{NO}_2$ に酸化される量との関係を表わしたグラフである。

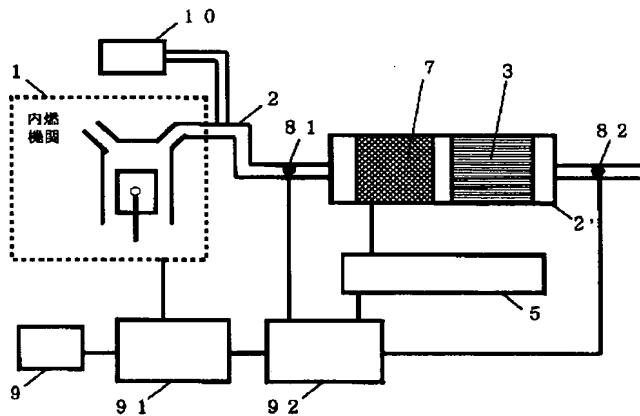
#### 【符号の説明】

- |   |      |
|---|------|
| 1 | 内燃機関 |
| 2 | 排気管  |

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- 2' 排気管ケース  
 3 触媒  
 4 電極  
 5 パルス高電圧発生装置  
 7 放電装置  
 8, 81, 82 温度計  
 9 センサー  
 91 内燃機関制御装置  
 92 第2内燃機関制御装置

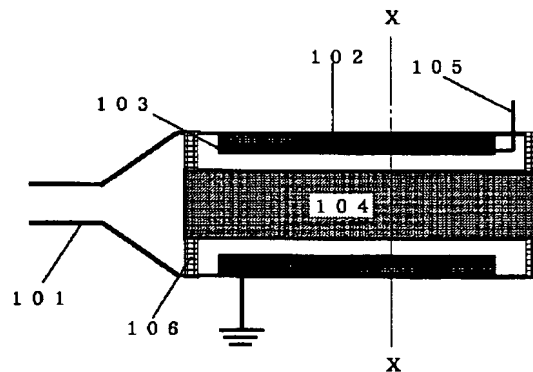
【図1】



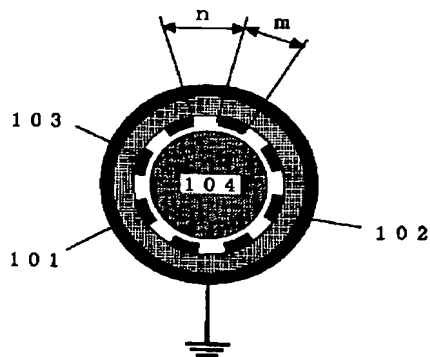
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- 93 易被毒劣化状態判定・制御手段  
 94 被毒劣化状態判定・制御手段  
 10 還元剤添加装置  
 101 排気管ケース  
 102 絶縁物  
 103 電極  
 104 スペース  
 105 プラグ  
 106 碍子

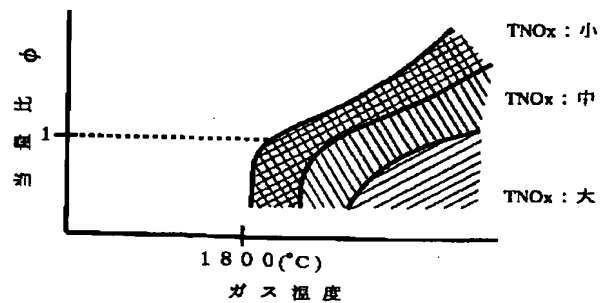
【図2】



【図3】



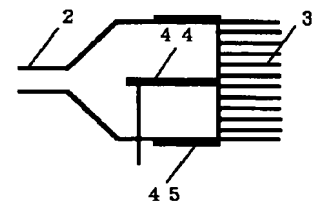
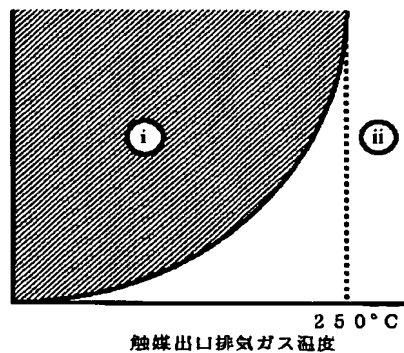
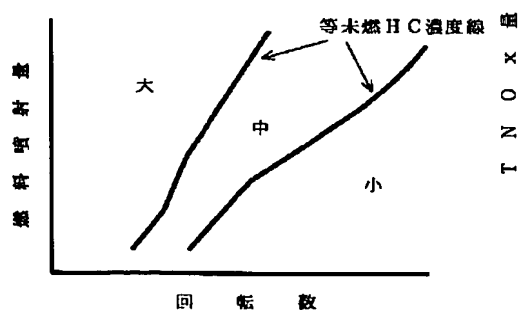
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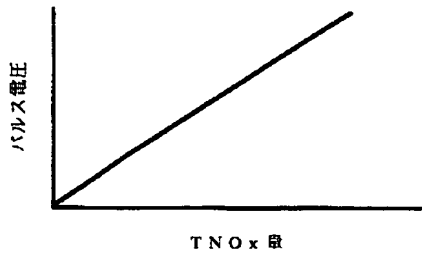
【図6】

【図10】

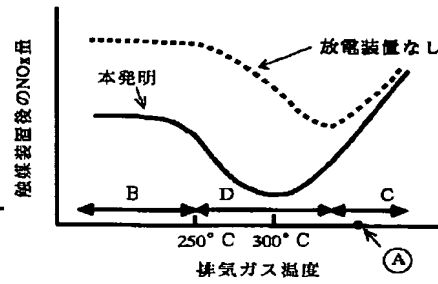
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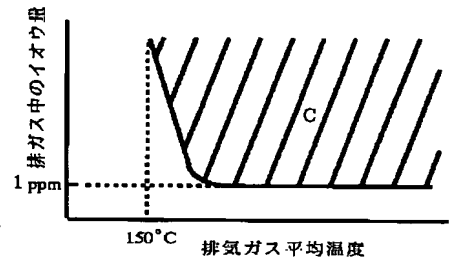
【図7】



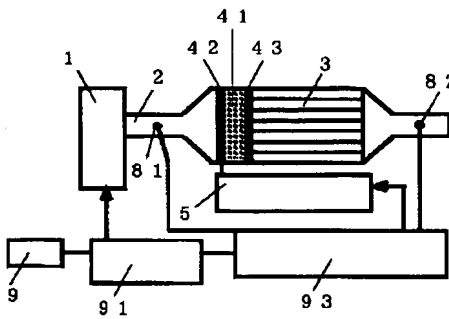
【図8】



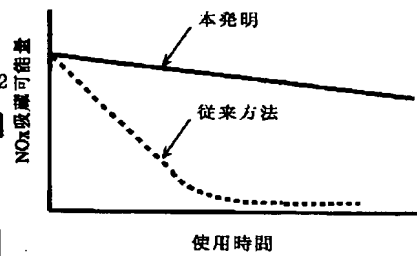
【図11】



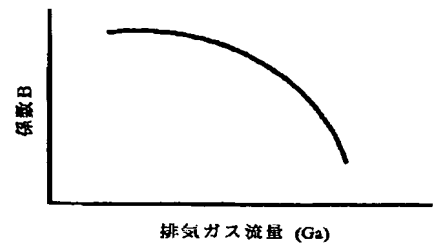
【図9】



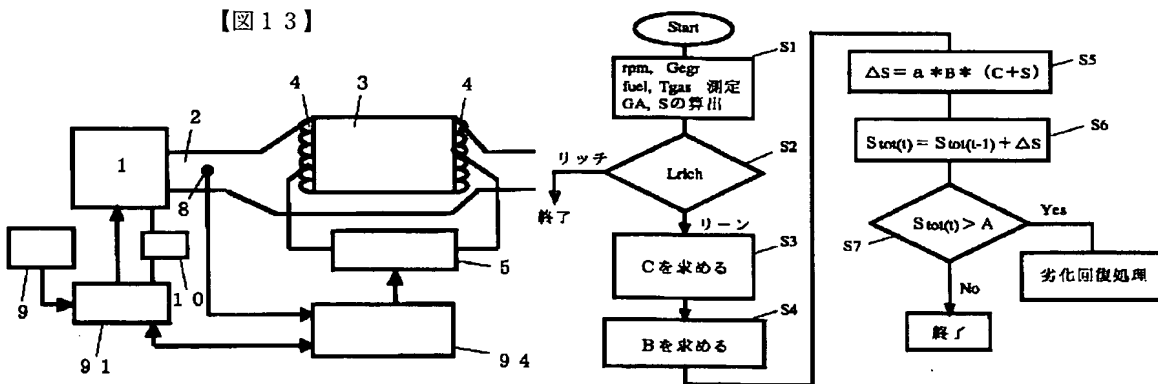
【図12】



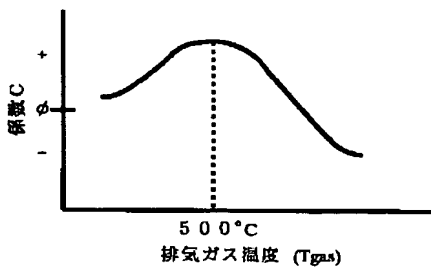
【図16】



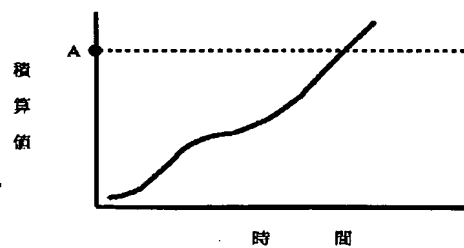
【図14】



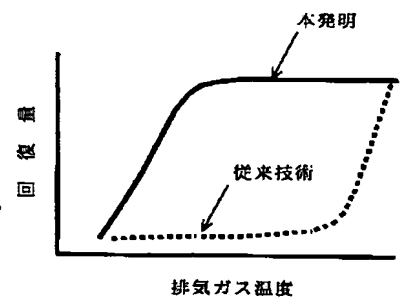
【図15】



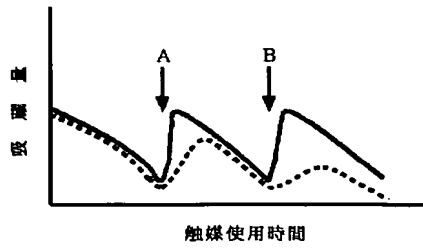
【図17】



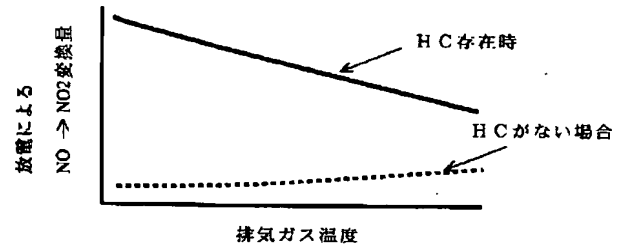
【図19】



【図 18】



【図 20】



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Fターム(参考) 3G091 AA11 AA18 AB05 AB06 AB14  
BA11 BA14 BA33 CA16 CA18  
DB10 DB13 EA01 EA03 EA05  
EA08 EA16 EA17 EA18 EA33  
FB10 FC02 HA07 HA36 HA37  
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4D048 AA06 AB02 AC02 BC01 BC10  
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